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# MODERN THERMODYNAMICS BY THE METHODS OF WILLARD GIBBS

BY  
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WITH A PREFACE BY  
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WITH 10 DIAGRAMS



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## PREFACE

THE science of thermodynamics, as a branch of mathematical physics founded on the First and Second Laws, was developed in an exact and comprehensive form by J. Willard Gibbs in his famous paper on "The Equilibrium of Heterogeneous Substances." No later writer on the subject has been able to improve on the elegance and generality of Gibbs' treatment. Although this work has been accessible in English, French and German for many years, its highly condensed and abstract form has repulsed the great majority of students, with the result that the science of thermodynamics has been recast in many different moulds during the last fifty years. To those acquainted with the power and beauty of Gibbs' treatment it has always been a source of regret that its outstanding merits have not become more widely known. Probably the reason is that no one has written a succinct and easily comprehensible book on Gibbsian lines. I consider it therefore of great importance that Mr. E. A. Guggenheim has undertaken to fill this lacuna, and that he has, in the present work, given to students of science an exact and yet very compendious account of thermodynamics as Gibbs conceived it. Mr. Guggenheim has, however, done much more than this, for he has dealt very fully with the subject of solutions and shown how the modern concepts and uses of fugacity, activity-coefficient, osmotic-coefficient, etc., which we owe to the important work of G. N. Lewis, J. N. Brønsted and N. Bjerrum, can be exactly related to the chemical potentials of Gibbs. This part of Mr. Guggenheim's book is extremely valuable, and, in combination with his classification of different types of solutions, brings order and clarity of thought into an important branch of physical chemistry that has suffered much in the past from obscurity and inexactitude.

Another part of the book where the author shows in like manner both clarity of thought and originality is to be found

in his treatment of electro-chemical cells and electro-chemical potentials. This is a very valuable contribution to science, and will certainly be welcomed by every student of physics and chemistry. The thermodynamical equations relating to osmotic, membrane and surface equilibria, equilibrium in a gravitational field, the Nernst Heat Theorem, and the thermodynamics of radiation, are all dealt with by the author in the same exact and logical manner, and all bear witness to the simplicity, power and elegance of Gibbs' methods.

I heartily commend Mr. Guggenheim's book to all students of physics and chemistry. They will find it an indispensable guide and lifelong friend, for age cannot wither the principles of thermodynamical science, enduring and incorruptible within their rightful domain.

F. G. DONNAN

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## AUTHOR'S PREFACE

**A**LTHOUGH text-books on thermodynamics are notably numerous, it is in only very few of them that any attempt is made to treat the subject as an exact science. There usually appears to be no reluctance to sacrifice exactness in an endeavour to make the treatment "elementary." The result is a collection of inaccurate relations between quantities incompletely or ambiguously defined.

For instance, a whole series of relations is given of the general type

$$\frac{dw}{dT} = - \frac{q}{T},$$

where  $w$  is the work done on the system in a given process,  $q$  the heat absorbed in the process, and  $T$  the absolute temperature. But the exact meaning of the operator  $d/dT$  is left ambiguous. A *given* process occurring at *various* temperatures is an ambiguous conception. One possible meaning is a process taking place between volume limits independent of the temperature; another a process taking place between pressure limits independent of the temperature; a third alternative is that the initial states at various temperatures are connected by a reversible adiabatic process and likewise the final states. In the last case only does the process at one temperature coupled with the reverse process at a different temperature constitute a Carnot cycle. The three possible cases mentioned correspond to different meanings of the operator  $d/dT$ , and consequently the exact significance of  $q$  must also be different. Yet it is usual to ignore such distinctions and confuse several different relations under one outward form. The deductions of these relations are often even more open to criticism than their forms. In the words of G. N. Lewis they are apt to involve "cyclical processes limping about eccentric and not quite completed cycles."

If these books have readers who consider such treatment as

just described a satisfactory method of making the subject "elementary," the present book is not intended for these. It has, on the contrary, been my aim to show how the analytical method, so elegantly developed by Willard Gibbs, leads in a simple and straightforward manner to relations that are unambiguous and exact. Whether this treatment is "elementary" or not is a question of terminology. At any rate, the only mathematical knowledge required from the reader is that of the simple differential calculus of functions of several variables, i.e. of partial differentiation. It is advisable that the reader should already be at least vaguely acquainted with the physical meaning of the first and second laws of thermodynamics, though not necessarily with their applications.

It will possibly appear to the reader that the statements of the first and second laws of thermodynamics are too brief. My excuse for this is that the discussion of the physical significance of these two laws given by Planck in his book "Thermodynamics" is so admirable that it should be read by every serious student of the subject. If I had been compelled to include an exhaustive treatment of the two laws satisfactory to myself, I should merely have had to copy or paraphrase Planck's treatment.

The two most valuable characteristic features of Willard Gibbs' method, which I have tried to the best of my ability to copy, are both completely absent from most text-books. The first is that he uses the exact straightforward analytical method instead of cycles which in almost all cases are either simple but inexact ("elementary") or exact but complicated. The second is the use of the "chemical potentials" denoted by  $\mu_i$ . These play the same fundamental part in determining chemical equilibria as does the temperature in determining thermal equilibrium and the pressure in determining mechanical equilibrium. These functions are indeed used in the Gibbsian manner in Lewis and Randall's "Thermodynamics," but under a name "partial molar free energies" which masks the fundamental nature of the functions. For an exact, straightforward and complete treatment of chemical equilibrium one could more readily dispense with the functions called free energy than with the chemical potentials. To emphasise the dependence of the latter on the former is in my opinion unfortunate.

Having described what I mean by "the methods of Willard Gibbs" in thermodynamics, I will explain my use of the epithet

"modern" in the title of this book. By it I refer to the inclusion of the exact treatment of solutions of the most general type. It is to G. N. Lewis that chemists are indebted for the introduction of the functions called "activity coefficients," by means of which the treatment of the most general type of solution can be made as elegant as that of the ideal solution. Another function of equal usefulness in this treatment is the "osmotic coefficient" introduced by Niels Bjerrum.

I have taken care to define the activity coefficients and osmotic coefficient in such a manner that they will always have the value unity in any ideal solution whether dilute or concentrated. The definitions given of these functions are not exactly equivalent to those used by their inventors, but seem to me to have the advantage that any deviation of their values from unity is a measure of deviations of the solution from ideality.

I have divided solutions into three classes, "ideal," "semi-ideal" and "non-ideal"; instead of the usual two. "Ideal" solutions are those in which the activity coefficients and osmotic coefficient are unity. "Semi-ideal" solutions are those in which the activity coefficients and osmotic coefficient are functions of the composition having values independent of the temperature and the pressure. In "non-ideal" solutions the values of the activity coefficients and the osmotic coefficient for a given composition depend on the temperature and the pressure. Contrary to common belief, semi-ideal solutions as well as ideal solutions mix at constant temperature and pressure without either volume change or heat effect.

The chapter entitled "extremely dilute" solutions contains a collection of familiar formulæ which are only approximate, and become inaccurate as soon as the mole fraction of any of the solute species becomes comparable to unity or that of the solvent becomes sensibly less than unity.

In the treatment of electrochemical systems I have shown how to avoid the use of functions which are not thermodynamically defined. Amongst these is the electric potential difference between two different phases unless either these are of identical composition or else they are both ideal solutions in the same solvent. Other examples are the individual ionic activity coefficients and the partition coefficient between two solvents of individual ionic species.

In the chapter on surfaces a section has been included dealing



with insoluble films, the interest in which has greatly increased of recent years.

Any comprehensive treatment of the so-called "third law of thermodynamics" belongs strictly to the realm of the statistical mechanics of the new quantum theory, and is beyond the range of pure thermodynamics. It is in fact impossible to give a purely thermodynamic formulation which at the same time is universally true, accurate and useful. The whole problem has been treated exhaustively by R. H. Fowler, and I have tried merely to summarise the thermodynamic formulæ corresponding to the conclusions deduced by him from quantum theory.

I have been fortunate in securing valuable advice and helpful criticism from several friends. Amongst these Professor R. H. Fowler has given me the benefit of his expert knowledge concerning the foundations of the laws of thermodynamics, and especially concerning the range of validity of the so-called third law. This last question I have also had the opportunity of discussing with Dr. J. L. Hoard. Dr. N. K. Adam and Dr. F. O. Koenig have helped me in clearing up several points in the treatment of surfaces. Mr. G. S. Hartley has made valuable suggestions concerning electro-chemical systems. To all of these I am most grateful. To Mr. B. Topley, who read the final proofs and prepared the index, I am especially indebted for the minute care with which he verified in detail every formula and every sentence. If, as I believe, the number of typographical errors is now very small, the credit is entirely his. I shall be grateful to any reader who informs me of any remaining errors. Last, but not least, I want to express my gratitude to Professor F. G. Donnan for the interest he has shown in the book at all stages of its preparation. Without his encouragement it might never have appeared in print.

As a good deal of alteration to the text has been carried out since the first proofs were printed, and it was not practicable to renumber all the formulæ at this stage, the numbering is not altogether logical. However, by use of the decimal notation it has been possible to keep the numbers in their natural order.

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## LIST OF MOST IMPORTANT SYMBOLS

$A$	Area of surface.
$A_i$	Partial molar area of species $i$ .
$C$	Heat capacity.
$C_P$	Heat capacity at constant pressure.
$C_V$	Heat capacity at constant volume.
$C_P$	Molar or mean molar heat capacity at constant pressure.
$C_V$	Molar or mean molar heat capacity at constant volume.
$C_{E1}$	Molar heat capacity at equilibrium with second phase.
$C_{\text{sat}}$	Molar heat capacity at saturation.
$C_{P_i}$ or $C_i$	Partial molar heat capacity at constant pressure of species $i$ .
$C_{V_i}$	Partial molar heat capacity at constant volume of species $i$ .
$C_i$	Volume concentration of species $i$ .
$E$	Total Energy.
$\bar{E} = E - \sum_{\sigma} \gamma^{\sigma} A^{\sigma}$	
$E$	Molar or mean molar energy ; also energy density of radiation.
$E_i$	Partial molar energy of species $i$ .
$\mathcal{E}$	Electromotive force.
$\mathcal{E}_{E1}$	Electrode potentials.
$\mathcal{E}_D$	Diffusion potential.
$\mathcal{E}_S$	Salt effect potential.
$F = E - TS$	Helmholtz free energy.
$\bar{F} = F - \sum_{\sigma} \gamma^{\sigma} A^{\sigma}$	
$F$	Molar or mean molar Helmholtz free energy ; also Helmholtz free energy density of radiation.
$F_i$	Partial molar Helmholtz free energy of species $i$ .
$\mathcal{F}$	Faraday.
$f$	Activity coefficient.
$f_{\pm}$	Mean activity coefficient of electrolyte.
$G = H - TS$	Gibbs free energy.
$\bar{G} = G - \sum_{\sigma} \gamma^{\sigma} A^{\sigma}$	
$G$	Molar or mean molar Gibbs free energy ; also Gibbs free energy density of radiation.
$G_i$	Partial molar Gibbs free energy of species $i$ .
$g$	Osmotic coefficient.
$H$	Heat content.
$\bar{H} = H - \sum_{\sigma} \gamma^{\sigma} A^{\sigma}$	

$H$	Molar or mean molar heat content.
$H_i$	Partial molar heat content of species $i$ .
$h$	Planck's constant.
$I$	Intensive property.
$i$	Chemical constant.
$J$	Extensive property.
$J$	Mean molar property.
$J_i$	Partial molar property of species $i$ .
$K, K', K'', K^*$	Equilibrium constant in various units.
$K_N$	Equilibrium mole fractions product.
$K_C$	Equilibrium concentrations product.
$k$	Constant of Henry's law.
$L_P$ or $L$	Heat of reaction at constant pressure.
$L_V$	Heat of reaction at constant volume.
$L_P$ or $L$	Molar heat of reaction at constant pressure.
$L_V$	Molar heat of reaction at constant volume.
$l_i$	Partition coefficient of species $i$ .
$l_{\pm}$	Mean partition coefficient of electrolyte.
$M$	Mass.
$M_i$	Molar mass (molecular weight) of species $i$ .
$m_i$	Molality of species $i$ .
$N$	Avogadro's number (number of molecules in a mole).
$n_i$	Number of moles of species $i$ .
$N_i$	Mole fraction of species $i$ .
$P$	Pressure.
$P^*$	Fugacity of single gas.
$p$	Vapour pressure of single component phase.
$p^*$	Fugacity of single component phase.
$p_i$	Partial vapour pressure of species $i$ .
$p_i^*$	(Partial) fugacity of species $i$ .
$Q_i$	Electric charge of species $i$ per mole.
$q$	Heat absorbed by system.
$q_+, q_-$	Number of cations and anions per mole of single electrolyte.
$R$	Gas constant.
$r$	Radius.
$S$	Entropy.
$S$	Molar or mean molar entropy ; also entropy density of radiation.
$S_i$	Partial molar entropy of species $i$ .
$T$	Temperature.
$T^\circ$	Freezing-point or boiling-point of pure solvent.
$t_i$	Transport number of species $i$ .
$V$	Volume.
$V$	Molar or mean molar volume.
$V_i$	Partial molar volume of species $i$ .
$V_i^*$	Partial molar volume at infinite dilution and zero pressure of species $i$ .
$w$	Work done on system.
$z_i$	Valency of ionic species $i$ .
$\alpha$	Stefan constant.

$\alpha$	Coefficient of thermal expansion.
$\Gamma_i$	Surface concentration of species $i$ .
$\gamma$	Surface tension.
$\gamma$	Ratio of $C_P$ to $C_V$ .
$\epsilon$	Efficiency.
$\epsilon$	Isothermal volume derivative of energy.
$\eta$	Isothermal pressure derivative of heat content.
$\theta$	Depression of freezing-point or rise of boiling-point.
$\kappa$	Isothermal compressibility, or compressibility coefficient.
$\kappa_S$	Adiabatic compressibility.
$\lambda_i$	Number of moles of species $i$ transferred.
$\mu_i$	Chemical potential of species $i$ .
$\bar{\mu}_i$	Electro-chemical potential of ionic species $i$ .
$\Pi$	Osmotic pressure.
$\Pi^\sigma$	Two-dimensional osmotic pressure.
$\varpi$	Statistical weight of lowest quantum state.
$\rho$	Density.
$\rho_1, \rho_2$	Principal radii of curvature.
$\sigma$	Symmetry number of molecule.
$\phi$	Gravitational potential.
$\psi$	Electric potential.

Suffices almost always refer to component species, e.g.  $p_i$  is partial vapour pressure of component species  $i$ . In particular:

$0$	refers to solvent species.
$s$	„ to solute species.
$R$ or $+$	„ to cation species.
$x$ or $-$	„ to anion species.
$\pm$	„ to mean value for ions of electrolyte.
$u$	„ to undissociated electrolyte species.
$j$	„ to all species other than species $i$ .

Suffices referring not to species but to processes are attached to the symbol  $L$ . Of these:

$D$	refers to dilution.
$E$	„ to evaporation or sublimation.
$F$	„ to fusion.
$S$	„ to solution.

Symbols in the index position usually refer to phases, e.g.  $\mu_i^\alpha$  is the chemical potential of the species  $i$  in the phase  $\alpha$ . Of these:

$\alpha, \beta$	refer to homogeneous phases.
$\sigma$	refers to surface phase.
$g$	„ to gas phase.
$l$	„ to liquid phase.
$s$	„ to solid phase.
$e$	„ to exterior.

$i$  refers to interior.

0 „ to pure solvent or infinite dilution.

The index 0 is also sometimes used to denote a term independent of the composition, and sometimes to denote the value at a given temperature such as  $T^\circ$  or the absolute zero.

An asterisk except in the symbols  $P^*$  and  $p^*$  denotes a term independent of the pressure as well as of the composition or a value at zero pressure and at infinite dilution.

The following operators are used :

$d$  Ordinary differential.

$\partial$   
 $\bar{\partial}$  Partial differential.

$D$  Differential at constant temperature and constant pressure, but varying composition.

$\Delta$  Excess of final over initial value.

$\Sigma$  Summation.

$\Sigma_+ \Sigma_-$  Summation over all cations or all anions.

$\int$  Integral.

# MODERN THERMODYNAMICS BY THE METHODS OF WILLARD GIBBS

## CHAPTER I

### INTRODUCTION AND FUNDAMENTAL LAWS

*Introduction.*—Thermodynamics, like classical Mechanics and classical Electromagnetism, is an exact mathematical science. Each such science may be based on a small finite number of premises or laws from which all the remaining laws of the science are deducible by purely logical reasoning. In the case of each of these sciences there is a certain amount of arbitrariness as to which of the laws one chooses as the premises from which the others are to be deduced.

In classical Mechanics, for instance, one might commence with Newton's laws of motion or alternatively one might use as the basis of the whole theory the Principle of Least Action. For an elementary exposition of the subject one would naturally choose the former, but to a reader already comparatively familiar with the subject the latter choice might be more æsthetically satisfying. Whichever one chooses for the development of the theory this basis postulates the existence and definiteness of certain measurable quantities. In the one case they may be distance, time, mass and force, in the other generalised co-ordinates, generalised momenta, time and energy. There is a common tendency to regard the conceptions of mass and force as more fundamental than those of generalised momenta and energy, and therefore to regard them as more natural "bricks" with which to build up the complete structure of classical Mechanics. But surely this is begging the question. When we first learn the elements of Mechanics we always do, in fact, commence by using mass and force as the "bricks". As a consequence of this they are the more familiar "bricks" and so, without pausing to think why they are more familiar, we are apt to regard them as the natural ones. Actually if we analyse the claim of mass to priority over energy and momentum, we find it due to the



accidental fact that we live in a very nearly constant gravitational field, as a consequence of which the mass of a body is proportional to its weight and so is readily measured with a common weighing machine. We would not dispute that Newton's laws are the best starting-point in the elementary teaching of classical Mechanics, but wish only to point out that the complete theory can be built up on other bases which, from a logical point of view, are equally solid. They may be less satisfactory practically and more so æsthetically.

Similarly, the classical theory of Electromagnetism is usually built up from conceptions such as electric and magnetic poles, dielectric constant and magnetic permeability. Without questioning the appropriateness of this choice for a first introduction to the subject, we would point out that from an æsthetic point of view the most satisfactory "bricks" with which to build the structure are the "four-potential" and "four-current" of the special relativity theory.

In the case of thermodynamics the situation is no different. It is customary to regard temperature, the measure of "hotness," as a natural "brick" and entropy, the measure of direction of change, as an unnatural one. This attitude is due to a feeling that temperature is more directly measurable. If, however, we analyse the question of how to measure temperature, we find a choice of two answers, neither of which is satisfactory:—

1. Measure it anyhow with any kind of "thermometer". We then obtain clumsy "unnatural" scales of temperature.

2. Measure it by means of a particular type of thermometer involving the use of a special kind of substance called a "perfect gas". We thus obtain a convenient and natural temperature scale known as the absolute scale. But if we ask what is a perfect gas and by what criterion are we to recognise one, the only answer obtainable without leaving the province of thermodynamics is that a perfect gas is a substance with certain properties, the most important of which is that when used as a thermometer it gives the convenient and natural temperature scale.

Obviously this kind of basis for an exact mathematical science is deplorable. This apparent vicious circle is due to an unconscious attempt to build up the structure without having chosen the most convenient "bricks". The usual definition of entropy is æsthetically unsatisfactory. For it is made dependent on the absolute temperature, a definition of which, independent of the postulate that certain substances make more perfect thermometers than others, involves conceptions, such as that of a Carnot cycle, which are at least as complex as that of entropy itself.

We have deliberately chosen to regard temperature and entropy, just as we regard pressure and volume, as two quantities both fundamental. We therefore do not attempt to define them in terms of other quantities regarded as simpler, for we do not admit the existence of simpler thermodynamic quantities. Nor do we attempt to define the one in terms of the other as we regard them as equally fundamental. We define them merely by their properties, expressed either in words or by mathematical symbols. After deriving the relationship between these quantities and other quantities, we shall return to a more detailed discussion of the least possible number of fundamental quantities to serve as the "bricks" of the structure.

*Thermodynamic System.*—A "thermodynamic system" is one whose interaction with its surroundings is partly thermal and partly mechanical (dynamic). Any conceivable interaction between the system and its surroundings consists of a flow of heat from the one to the other and the performance of work by the one on the other.

*Thermodynamic Process.*—If on comparing the state of a thermodynamic system at two different times it is found that there is a difference in any macroscopic property of the system, then we say that between the two times of observation a "process" has taken place. If, for example, two equal quantities of gas are allowed to intermix, this will constitute a "process" from a thermodynamic point of view provided the two initially separate gases are distinguishable by any macroscopic property, even though their difference is very slight, as, for example, might be the case for two isotopes. If, on the other hand, the two initially separate gases are not distinguishable by any macroscopic property, then from a thermodynamic point of view no "process" takes place, although from a molecular standpoint there is a never-ceasing intermixing.

*Infinitesimal Process.*—A process taking place to such an extent that there is only an infinitesimal change in any of the macroscopic properties of a system is called an "infinitesimal process."

*Energy and First Law of Thermodynamics.*—There exists a function of the state of any thermodynamic system called its "energy" (or "total energy") with the following property: In any process the sum of the heat  $q$  absorbed by the system from its surroundings and the work  $w$  done on the system by its surroundings is equal to the increase of the energy  $E$  of the system. For any infinitesimal process we write this

$$q + w = dE, \quad (1)$$

and for any finite process

$$q + w = \Delta E, \quad (2)$$

where the operator  $\Delta$  denotes the excess of final over initial value.

Actually, according to the above definition, represented by the relations (1) and (2), the energy is indefinite to the extent of an arbitrary additive constant, but this indefiniteness is of no practical consequence. Any relation between the energy and other quantities, representing something observable, will always involve the value of a change in the energy, and this will be independent of the arbitrary additive constant. If desired, the arbitrariness can be entirely removed by defining the energy as having some specific value, say zero, in some completely defined state of the system.

It need hardly be mentioned that in formulæ (1) and (2) the energy  $E$ , the heat absorbed  $q$  and the work  $w$  done on the system must be measured in the same units. It does not matter if these are mechanical units such as ergs and joules, or thermal units such as calories.

The law contained in (1) and (2) is known as the "First Law of Thermodynamics". It is nothing more than an extension of the mechanical principle of "The Conservation of Energy" to include "thermal energy" or "heat". This law was stated in its present unambiguous form by Helmholtz (1847). Its content is, however, already contained implicitly in a posthumous publication of Carnot (died 1832), and also in the work of Mayer (1842).

In a cycle, which leaves the system in the same final state as its initial state, obviously

$$\Delta E = 0. \quad (3)$$

It follows that for any complete cycle

$$q + w = 0. \quad (4)$$

*Natural, Unnatural and Reversible Processes.*—All the independent infinitesimal processes that might conceivably take place may be resolved into three kinds: "natural" processes, "unnatural" processes and "reversible" processes. "Natural" processes are all such as actually do occur in nature; examples are the interdiffusion of two gases, the equalisation of pressures and in general any approach towards complete equilibrium. An "unnatural" infinitesimal process is one that is the exact opposite of some natural infinitesimal process; they never occur in nature. As a limiting case between natural and unnatural

processes we have "reversible" processes: they consist of a passage of a system in either direction through a continuous series of states of equilibrium. Reversible processes do not actually occur in nature, but, in whichever direction we contemplate a reversible process, we can by an infinitesimal alteration of the conditions produce a natural process differing only infinitesimally from the reversible process contemplated. An example is the movement of a piston separating two gases at equal pressures: actually it will not move, but by an infinitesimal alteration of the pressure of either gas we could make it move in either direction.

*Temperature.*—The "temperature" of a system is a function of its state with the qualitative property of determining the direction of flow of heat. The flow of heat from a higher to a lower temperature (unaccompanied by other change) is a natural process; the reverse is an unnatural process. In a reversible process any flow of heat must be at constant temperature. Quantitatively temperature can be measured on an infinite number of different scales, but temperature as measured on one particular scale called the "absolute" scale has particularly simple properties, which will be described below in connection with entropy. The temperature as measured on this scale is always positive.

*Entropy and Second Law of Thermodynamics.*—There exists a function  $S$  of the state of a system called the "entropy" of the system with the following properties: If for any infinitesimal change in a system the heat absorbed from the surroundings is  $q$ , then

$$\frac{q}{T_{\max}} < dS \quad \text{for any natural process,} \quad (5.1)$$

$$\frac{q}{T_{\min}} > dS \quad \text{for any unnatural process,} \quad (5.2)$$

$$\frac{q}{T} = dS \quad \text{for any reversible process,} \quad (6)$$

where  $T_{\max}$  denotes the highest value of the temperature in any part of the system,  $T_{\min}$  denotes the lowest value of the temperature in any part of the system. In the case of a reversible process the temperature must be the same throughout the system, otherwise the system would not be in equilibrium, and so the process could not be reversible. Hence in (6)  $T$  denotes the temperature of the whole system.

These relations are a statement of the law known as the "Second Law of Thermodynamics". It is to be noted that in

this formulation the absolute temperature  $T$  and the entropy  $S$  are introduced simultaneously as two fundamental quantities with the properties given by the relations (5) and (6).

The Second Law of Thermodynamics was foreshadowed by the work of Carnot (1824), but was first clearly enunciated by Clausius (1850), to whom is also due the conception of entropy. The absolute scale of temperature is due to Kelvin (1848), who enunciated the Second Law of Thermodynamics independently of Clausius (1851).

According to (5) and (6) only changes in  $S$  are defined, not  $S$  itself. The entropy is thus indefinite to the extent of an arbitrary additive constant. This is, however, of no consequence, as only entropy changes are ever of any physical significance. If desired, the arbitrariness can be removed by assigning some specific value, say zero, to the entropy of the system in some completely defined state.

For a finite process the relations (5) and (6) hold for each of the infinitesimal steps into which the finite process may be divided. In particular, for a process reversible throughout

$$\sum \frac{q}{T} = \Delta S, \quad (7)$$

and for a reversible cycle, which leaves the system in a final state identical with its initial state

$$\sum \frac{q}{T} = 0. \quad (8)$$

*Carnot Cycle.*—An example of a reversible cycle is the cycle associated with the name of Carnot (1824). This cycle is of great historical importance in the evolution of thermodynamics. The Carnot cycle consists of four steps, two of them at constant temperature (isothermal), the other two without gain or loss of heat by the system (adiabatic). The isothermal steps and the adiabatic ones alternate. For example, suppose we have first a change at constant temperature  $T_1$  (isothermal change) with absorption of heat  $q_1$  by the system from a heat reservoir at the temperature  $T_1$ ; secondly, a change of temperature from  $T_1$  to  $T_2$  without gain or loss of heat (adiabatic change); thirdly, another isothermal change at temperature  $T_2$  with absorption of heat  $q_2$  from a heat reservoir, also at the temperature  $T_2$ ; fourthly, another adiabatic change restoring the system to its original state. It is to be noticed that in each of the isothermal steps the reservoir must have the same temperature as the system, otherwise the heat exchange would not be reversible. Forming

the sum of  $\frac{q}{T}$  for the four steps we have

$$\frac{q_1}{T_1} + 0 + \frac{q_2}{T_2} + 0 = 0, \quad (9)$$

or

$$\frac{q_1}{T_1} = -\frac{q_2}{T_2}. \quad (10)$$

Since the temperature is always positive, we see from (10) that  $q_1$  and  $q_2$  are of opposite sign, so that at the one temperature heat is absorbed from the reservoir (source), while at the other temperature heat is lost to the reservoir (sink). The absolute magnitudes of these two quantities of heat are proportional to the absolute temperature of the source and sink respectively.

The Carnot cycle, being reversible, can of course be worked either way round. For the sake of definiteness let us suppose that the system absorbs heat at the higher temperature, say  $T_1$ , and loses heat at the lower temperature  $T_2$ . Then, as we are assuming that

$$T_1 > T_2, \quad (11)$$

it follows from (10) that

$$q_1 > -q_2, \quad (12)$$

or

$$q_1 > |q_2|. \quad (13)$$

The total work  $w$  done on the system in the cycle is according to (4) given by

$$w = -(q_1 + q_2) = -(q_1 - |q_2|) < 0. \quad (14)$$

That is to say, that a net amount of work  $q_1 - |q_2|$  is done by the system on the surroundings. The total energy changes during the cycle may be described as follows: A quantity of heat  $q_1$  is absorbed at the higher temperature  $T_1$ ; of this the fraction  $q_1 \frac{T_2}{T_1}$  is given up again at the lower temperature  $T_2$ , the re-

mainder  $q_1 \frac{T_1 - T_2}{T_1}$  being converted to work done by the system on the surroundings. The efficiency  $\epsilon$  of the cycle is defined as the fraction of heat taken in from the source that is converted into work, the remainder being given out to the sink. In the case of a Carnot cycle the efficiency is given by

$$\epsilon = \frac{T_1 - T_2}{T_1}. \quad (15)$$

We see that the smaller  $T_2$  the greater the efficiency  $\epsilon$ . As the temperature is always positive the maximum possible efficiency is unity, and this is attained only when the temperature of the sink is absolute zero ( $T_2 = 0$ ).

*Phases.*—The simplest and most important kind of thermodynamic system may be considered as consisting of a finite number of homogeneous parts called "phases." Strictly, we should also include a finite number of non-homogeneous parts forming the boundaries between various pairs of homogeneous phases. However, for many purposes these non-homogeneous parts are of such small extent compared with the homogeneous parts that they may be ignored. We shall for the sake of simplicity so ignore them for the time being. At a later stage we shall show how we may take account of them in an exact manner.

*Extensive Properties.*—The mass of a system is clearly equal to the sum of the masses of its constituent phases. Any property, such as mass, whose value for the whole system is equal to the sum of its values for the separate phases is called an "extensive property" or a "capacity factor."

Important examples of extensive properties are the energy  $E$ , the entropy  $S$  and the volume  $V$ . The energy  $E$  of a system is related to the energies  $E^\alpha$  of the separate phases  $\alpha$  by

$$E = \sum_{\alpha} E^{\alpha}. \quad (16.1)$$

Similarly, for the entropy, we have

$$S = \sum_{\alpha} S^{\alpha}, \quad (16.2)$$

and for the volume

$$V = \sum_{\alpha} V^{\alpha}. \quad (16.3)$$

*Intensive Properties.*—The density of a phase is clearly constant throughout the phase, because the phase is by definition homogeneous. Further, the density of a phase of a given kind and state is independent of the quantity of the phase. Any property of a phase with these characteristics is called an "intensive property" or an "intensity factor."

The temperature  $T^\alpha$  and the pressure  $P^\alpha$  are important examples of intensive properties.

*Pressure of Phase.*—The fundamental property of the pressure is familiar from the science of hydrostatics, and may be expressed by the statement that for any infinitesimal change  $dV^\alpha$  of the volume of the phase  $\alpha$  the work  $w^\alpha$  done on the phase is given by

$$w^\alpha = -P^\alpha dV^\alpha, \quad (17)$$

where  $P^\alpha$  is the pressure of the phase  $\alpha$ .

*Chemical Content of Phase.*—The chemical content of a phase is defined by the number  $n_i^\alpha$  of units of quantity of each of a finite number of independently variable chemical species in the phase. The unit of quantity may be the gramme or any other unit of mass. It need not necessarily be the same mass for different chemical species. In fact, it is most usual to take as units of quantity the gramme-molecule or mole, that is a mass proportional to that given by the accepted chemical formula of the particular species. A thermodynamic definition of the mole will be derived later. In anticipation of this we may take the mole as the unit of quantity for each chemical species.

*Complete Description of Phase.*—If we know the volume and chemical content of a phase, we still have not a complete description of it. For the phase might be able to absorb or lose heat without change of volume or chemical content. Therefore, for the complete description of a chemical phase it is necessary to fix one other variable besides the volume  $V^\alpha$  and the number of moles  $n_i^\alpha$  of the various chemical species  $i$ . For this last independent variable we might choose the pressure  $P^\alpha$  or the energy  $E^\alpha$  or the temperature  $T^\alpha$  or the entropy  $S^\alpha$ . For reasons that will appear later it is most convenient initially to choose the entropy  $S^\alpha$ .

For any phase  $\alpha$  we may then regard any of its properties as a function of the independent variables  $S^\alpha$ ,  $V^\alpha$  and the  $n_i^\alpha$ . In particular, the energy  $E^\alpha$  may be regarded as a function of  $S^\alpha$ ,  $V^\alpha$  and the  $n_i^\alpha$ . Hence, for any variation in the state or composition of the phase, we have

$$dE^\alpha = \left(\frac{\partial E^\alpha}{\partial S^\alpha}\right)_{V^\alpha, n_i^\alpha} dS^\alpha + \left(\frac{\partial E^\alpha}{\partial V^\alpha}\right)_{S^\alpha, n_i^\alpha} dV^\alpha + \sum_i \left(\frac{\partial E^\alpha}{\partial n_i^\alpha}\right)_{S^\alpha, V^\alpha, n_j^\alpha} dn_i^\alpha, \quad (18\cdot1)$$

where the suffix  $n_i^\alpha$  denotes all the quantities of the type  $n_i^\alpha$  except  $n_i^\alpha$  itself.

*Changes at Constant Composition.*—If we restrict ourselves to changes in a single phase  $\alpha$  taking place without any alteration of composition, then (18·1) becomes

$$dE^\alpha = \left(\frac{\partial E^\alpha}{\partial S^\alpha}\right)_{V^\alpha, n_i^\alpha} dS^\alpha + \left(\frac{\partial E^\alpha}{\partial V^\alpha}\right)_{S^\alpha, n_i^\alpha} dV^\alpha, \quad (18\cdot2)$$

and such a change can consist only of an exchange of heat with the surroundings and work done on or by the surroundings. If the phase  $\alpha$  is in thermal and mechanical equilibrium with its



surroundings, this change will be reversible and so the heat  $q^\alpha$  absorbed from the surroundings will, according to (6), be given by

$$q^\alpha = TdS^\alpha, \quad (18.3)$$

where  $T$  is the temperature of both the phase  $\alpha$  and its surroundings. Similarly, the work  $w^\alpha$  done on the system by the surroundings will be given by

$$w^\alpha = -PdV^\alpha, \quad (18.4)$$

where  $P$  is the pressure of both the phase  $\alpha$  and its surroundings. Hence, by the first law of thermodynamics (1)

$$dE^\alpha = TdS^\alpha - PdV^\alpha. \quad (18.5)$$

But according to (18.1) the coefficients of  $dS^\alpha$  and  $dV^\alpha$  are functions only of the state of the phase  $\alpha$  and not of the surroundings. Hence formula (18.5) holds true even if the phase  $\alpha$  is not in thermal and mechanical equilibrium with its surroundings, but  $T$  and  $P$  are then the temperature  $T^\alpha$  and pressure  $P^\alpha$  of the phase  $\alpha$  and not those of the surroundings.

Comparing (18.5) with (18.1), we see that for the most general variation of the phase  $\alpha$

$$dE^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i \left( \frac{\partial E^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} dn_i^\alpha. \quad (18.6)$$

*Chemical Potentials.*—The treatment of all kinds of chemical equilibria or equilibria involving changes in the chemical content of one or more phases is considerably simplified by making use of the functions called the "chemical potentials." Their use is due to Willard Gibbs (1875). The chemical potential  $\mu_i^\alpha$  of the chemical species  $i$  in the phase  $\alpha$  may be defined by

$$\mu_i^\alpha = \left( \frac{\partial E^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} \quad (19)$$

where  $n_j^\alpha$  denotes all the quantities of the type  $n_i^\alpha$  except  $n_i^\alpha$  itself.

Substituting (19) into (18.6) we obtain

$$dE^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha. \quad (20.0)$$

This is equivalent to the relations

$$\left( \frac{\partial E^\alpha}{\partial S^\alpha} \right)_{V^\alpha, n_i^\alpha} = T^\alpha, \quad (20.1)$$

$$\left( \frac{\partial E^\alpha}{\partial V^\alpha} \right)_{S^\alpha, n_i^\alpha} = -P^\alpha, \quad (20.2)$$

$$\left( \frac{\partial E^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} = \mu_i^\alpha. \quad (20.3)$$

From a purely thermodynamic point of view we may regard the equations (20) as defining  $T^\alpha$ ,  $P^\alpha$  and the  $\mu_i^\alpha$  in terms of  $E^\alpha$ ,  $S^\alpha$ ,  $V^\alpha$  and the  $n_i^\alpha$ .

*Change of Notation.*—In formulæ such as those of the last paragraph we can without serious risk of ambiguity omit the indices  $\alpha$ . Thus we may write

$$dE = TdS - PdV + \sum_i \mu_i dn_i, \quad (20.4)$$

instead of (20.0) in order to simplify the notation. The indices referring to separate phases will be inserted only where necessary to avoid ambiguity.

*Other Thermodynamic Functions.*—It is often more convenient to treat the pressure instead of the volume of each phase as an independent variable. In this case a more useful function than the energy  $E$  is the "heat content" or "total heat"  $H$  defined for each phase by

$$H = E + PV, \quad (21)$$

using the abbreviated notation of the last paragraph.

Differentiating (21) and combining with (20.4), we get

$$dH = TdS + VdP + \sum_i \mu_i dn_i, \quad (22)$$

whence

$$\left(\frac{\partial H}{\partial S}\right)_{P, n_i} = T, \quad (23.1)$$

$$\left(\frac{\partial H}{\partial P}\right)_{S, n_i} = V, \quad (23.2)$$

$$\left(\frac{\partial H}{\partial n_i}\right)_{S, P, n_j} = \mu_i. \quad (23.3)$$

Again, it is usually more convenient to regard the temperature than the entropy as an independent variable defining the state of each phase. In this case, of more fundamental importance than the energy  $E$  and the heat content  $H$  are the functions  $F$  and  $G$  defined respectively for each phase by

$$F = E - TS, \quad (24)$$

$$G = H - TS. \quad (25)$$

The function  $F$  is due to Helmholtz, and was named by him the "free energy." It is sometimes referred to as the "work function." It was called by Gibbs the "force function for constant temperature." The function  $G$  is due to Gibbs, and is often referred to by modern writers as the "free energy." We shall call  $F$  the "Helmholtz free energy" and  $G$  the "Gibbs free

energy." But to avoid any possibility of confusion we shall always refer directly to the symbols  $F$  and  $G$  defined according to (24) and (25).

Differentiation of (24) and comparison with (20.4) gives

$$dF = -SdT - PdV + \sum_i \mu_i dn_i, \quad (26)$$

or

$$\left(\frac{\partial F}{\partial T}\right)_{V, n_i} = -S, \quad (27.1)$$

$$\left(\frac{\partial F}{\partial V}\right)_{T, n_i} = -P, \quad (27.2)$$

$$\left(\frac{\partial F}{\partial n_i}\right)_{T, V, n_j} = \mu_i. \quad (27.3)$$

Similarly, differentiation of (25) and comparison with (20.4) gives

$$dG = -SdT + VdP + \sum_i \mu_i dn_i, \quad (28)$$

or

$$\left(\frac{\partial G}{\partial T}\right)_{P, n_i} = -S, \quad (29.1)$$

$$\left(\frac{\partial G}{\partial P}\right)_{T, n_i} = V, \quad (29.2)$$

$$\left(\frac{\partial G}{\partial n_i}\right)_{T, P, n_j} = \mu_i. \quad (29.3)$$

Since  $E$  and  $S$  are indefinite to the extent of an arbitrary additive constant, it follows that the same applies to  $H$ . On the other hand,  $F$ ,  $G$  and the  $\mu_i$  are arbitrary to the extent of an arbitrary additive constant and an additive term of the form  $aT$  where  $a$  is an arbitrary constant. The functions  $F$ ,  $G$  and the  $\mu_i$  are, however, of physical importance only for the discussion of isothermal changes, and for these  $\Delta F$ ,  $\Delta G$  and the  $\Delta\mu_i$  are completely defined.

*Mutually Independent Fundamental Quantities.*—We are now in a position to consider which of the thermodynamic quantities can conveniently be chosen as the fundamental "bricks" from which the whole structure may be built, and in terms of which all other thermodynamic quantities are definable. We have already pointed out that formulæ (20) may be regarded as defining  $T$ ,  $P$  and the  $\mu_i$  in terms of  $E$ ,  $S$ ,  $V$  and the  $n_i$ . Similarly, we might regard (23) as defining  $T$ ,  $V$  and the  $\mu_i$  in terms of  $H$ ,  $S$ ,  $P$  and the  $n_i$ ; or (27) as defining  $S$ ,  $P$  and the  $\mu_i$  in terms of  $F$ ,  $T$ ,  $V$  and the  $n_i$ ; or (29) as defining  $S$ ,  $V$  and the  $\mu_i$  in

terms of  $G$ ,  $T$ ,  $P$  and the  $n_i$ . From a logical point of view, there is nothing to choose between the four sets

$$(1) E, S, V, n_i,$$

$$(2) H, S, P, n_i,$$

$$(3) F, T, V, n_i,$$

$$(4) G, T, P, n_i,$$

as choice of fundamental quantities.

The quantity  $E$  regarded as a function of  $S$ ,  $V$  and the  $n_i$  is called the "characteristic function" corresponding to this choice of independent variables. The values of all the other thermodynamic functions can be expressed in terms of the characteristic function  $E$  and its differential coefficients with respect to  $S$ ,  $V$  and the  $n_i$ .

Similarly,  $H$  regarded as a function of  $S$ ,  $P$  and the  $n_i$  is the "characteristic function" corresponding to this choice of independent variables. A third alternative is to choose as "characteristic function"  $F$  with the independent variables  $T$ ,  $V$  and the  $n_i$ . The last, and in many ways the most convenient choice, is to take as independent variables  $T$ ,  $P$  and the  $n_i$ , in which case the corresponding "characteristic function" is  $G$ .

To illustrate how all the thermodynamic functions may be expressed in terms of the characteristic function and its derivatives with respect to the corresponding independent variables, we shall tabulate the formulæ for the set  $G$ ,  $T$ ,  $P$ ,  $n_i$ . We have

$$S = - \frac{\partial G}{\partial T}, \quad (30.1)$$

$$H = G + TS = G - T \frac{\partial G}{\partial T}, \quad (30.2)$$

$$V = \frac{\partial G}{\partial P}, \quad (30.3)$$

$$F = G - PV = G - P \frac{\partial G}{\partial P}, \quad (30.4)$$

$$E = G + TS - PV = G - T \frac{\partial G}{\partial T} - P \frac{\partial G}{\partial P}, \quad (30.5)$$

$$\mu_i = \frac{\partial G}{\partial n_i}. \quad (30.6)$$

If it is desired to choose the temperature, but not the entropy as one of the fundamental quantities, then of the other fundamental quantities there should be chosen as characteristic function not the total energy  $E$ , but one of the free energies  $F$  or  $G$ ,

according as  $V$  or  $P$  is also chosen as fundamental. The customary choice of fundamental quantities in elementary textbooks

$$E, T, V, n_i,$$

is unfortunate, as the entropy cannot be defined as an algebraic function of these quantities and their differential coefficients with respect to one another. The quantity entropy thereby acquires an appearance of artificiality in no way justifiable.

*Intensity Factors and Capacity Factors.*—There is a certain one-to-one relationship between the pairs of functions

$$(1) \ T \text{ and } S,$$

$$(2) \ P \text{ and } V,$$

$$(3) \ \mu_i \text{ and } n_i,$$

the first member of each pair being an intensity factor, the second a capacity factor. The product of the two members of each pair has the dimensions of an energy. The relationship is most clearly shown by the formulæ (20), which define the intensity factors  $T$ ,  $P$ ,  $\mu_i$  in terms of the capacity factors  $S$ ,  $V$ ,  $n_i$ .

*Units and Dimensions.*—As already mentioned, it is usual to measure  $n_i$  in moles and so  $\mu_i$  in energy units per mole. Since the product of pressure and volume has the dimension of an energy, we choose as unit of pressure the unit of energy divided by the unit of volume.

The unit of  $T$  and that of  $S$  are not independent, but are related by the condition that their product must be equal to the unit of energy. It is usual to fix the unit of temperature such that the difference between the temperatures of water boiling under a pressure of one atmosphere and water freezing under a pressure of one atmosphere is equal to one hundred units. This unit of temperature is called the centigrade degree. If the unit of energy is the calorie, that of entropy is the calorie per degree centigrade. According to their definitions it is clear that the heat content  $H$ , the Helmholtz free energy  $F$  and the Gibbs free energy  $G$  have the dimension of energy and are therefore measured in energy units.

*Gibbs-Duhem Relation.*—All the formulæ (20.4), (22), (26), (28) are homogeneous and of first degree in all the capacity factors. It is therefore possible to integrate them for constant values of the intensity factors. This operation corresponds mathematically to applying Euler's theorem and physically to increasing the quantity of the system without altering its nature. All four relations, when integrated, lead to the same result

$$G = E - TS + PV = \sum_i \mu_i n_i. \quad (31)$$

Differentiating (31) and comparing with (28) we get

$$-SdT + VdP - \sum_i n_i d\mu_i = 0. \quad (32)$$

The most important special case of this is

$$dT = 0 \quad dP = 0 \quad \sum_i n_i d\mu_i = 0, \quad (33)$$

a relation between the variations of the chemical potentials of the various components of a system, when the composition is varied at constant temperature and pressure. This important relation is known as the "Gibbs-Duhem formula".

*Infinitesimal Adiabatic Changes.*—If an infinitesimal change takes place in a system thermally insulated (adiabatic change) the heat absorbed  $q$  is zero. The work  $w$  done on the system will, according to (1), be equal to  $dE$ , the increase in the energy of the system. We therefore have, according to (5) and (6):

for a natural process

$$dE = w \quad dS > 0, \quad (34.1)$$

for an unnatural process

$$dE = w \quad dS < 0, \quad (34.2)$$

for a reversible process

$$dE = w \quad dS = 0. \quad (34.3)$$

If in particular the change takes place at constant volume, the work done on the system is zero, and we therefore have the set of conditions:

for a natural process

$$dE = 0 \quad dV = 0 \quad dS > 0, \quad (35.1)$$

for an unnatural process

$$dE = 0 \quad dV = 0 \quad dS < 0, \quad (35.2)$$

for a reversible process

$$dE = 0 \quad dV = 0 \quad dS = 0. \quad (35.3)$$

If, on the other hand, the system is kept not at constant volume but at constant pressure during the infinitesimal change, the work  $w$  done on the system is given by

$$w = dE = -PdV = -d(PV), \quad (36)$$

so that by (21)

$$dH = dE + d(PV) = 0. \quad (37)$$

We then have the set of conditions :

for a natural process

$$dH = 0 \quad dP = 0 \quad dS > 0, \quad (38.1)$$

for an unnatural process

$$dH = 0 \quad dP = 0 \quad dS < 0, \quad (38.2)$$

for a reversible process

$$dH = 0 \quad dP = 0 \quad dS = 0. \quad (38.3)$$

*Infinitesimal Isothermal Changes.*—Instead of a thermally insulated system, let us now consider one whose temperature is kept constant at the value  $T$ . This may be achieved by keeping the system in a large bath at the temperature  $T$ . This bath may be supposed to give heat to the system or abstract heat from it so as to maintain the temperature of the system constant (isothermal change). If the bath is sufficiently large it will be able to do this without any appreciable change in its own temperature. Under these conditions the heat interchange between system and bath will be reversible. If  $S$  denotes the entropy of the system and  $S'$  that of the bath, then, according to (5) and (6), we have the conditions :

for a natural process

$$dT = 0 \quad dS + dS' > 0, \quad (39.1)$$

for an unnatural process

$$dT = 0 \quad dS + dS' < 0, \quad (39.2)$$

for a reversible process

$$dT = 0 \quad dS + dS' = 0. \quad (39.3)$$

But as the heat exchange between the system and the bath is by supposition reversible, we have, for the entropy increase  $dS'$  of the bath

$$dS' = -\frac{q}{T}, \quad (40)$$

where  $q$  is the heat absorbed by the system from the bath. Combining (40) with the first law of thermodynamics (1), we have

$$dS' = -\frac{dE}{T} + \frac{w}{T}. \quad (41)$$

Hence in place of (39) we have the conditions :

for a natural process

$$dT = 0 \quad dS - \frac{dE}{T} + \frac{w}{T} > 0, \quad (42.1)$$

for an unnatural process

$$dT = 0 \quad dS - \frac{dE}{T} + \frac{w}{T} < 0, \quad (42.2)$$

for a reversible process

$$dT = 0 \quad dS - \frac{dE}{T} + \frac{w}{T} = 0. \quad (42.3)$$

According to the definition (24) of  $F$ , these may be written :  
for a natural process

$$dT = 0 \quad dF < w, \quad (43.1)$$

for an unnatural process

$$dT = 0 \quad dF > w, \quad (43.2)$$

for a reversible process

$$dT = 0 \quad dF = w. \quad (43.3)$$

If in particular we consider a change at constant volume, the work done  $w$  is zero, and consequently we have the conditions :  
for a natural process

$$dT = 0 \quad dV = 0 \quad dF < 0, \quad (44.1)$$

for an unnatural process

$$dT = 0 \quad dV = 0 \quad dF > 0, \quad (44.2)$$

for a reversible process

$$dT = 0 \quad dV = 0 \quad dF = 0. \quad (44.3)$$

If, on the other hand, we suppose not the volume but the pressure of the system to be kept constant, we have for the work  $w$  done on the system

$$w = -PdV = -d(PV). \quad (45)$$

But according to the relations (21), (24), (25)

$$dG = dF + d(PV) = dF - w, \quad (46)$$

and so the conditions become :

for a natural process

$$dT = 0 \quad dP = 0 \quad dG < 0, \quad (47.1)$$

for an unnatural process

$$dT = 0 \quad dP = 0 \quad dG > 0, \quad (47.2)$$

for a reversible process

$$dT = 0 \quad dP = 0 \quad dG = 0. \quad (47.3)$$



*Equilibrium Conditions. General Form.*—If a system is in complete equilibrium, any conceivable infinitesimal change in it must be reversible. For a natural process is an approach towards equilibrium, and as the system is already in equilibrium the change cannot be a natural one. Nor can it be an unnatural one, for in that case the opposite infinitesimal change would be a natural one, and this would contradict the supposition that the system is already in equilibrium. The only remaining possibility is that any conceivable infinitesimal change must be reversible if the system is in complete equilibrium. If we first consider an infinitesimal change at constant volume, the system being thermally insulated, we have, according to (35.3), the equilibrium conditions

$$dS = 0 \quad dV = 0 \quad dE = 0. \quad (48)$$

If, on the other hand, we consider an infinitesimal change at constant pressure, the system being thermally insulated, we have, according to (38.3), the equilibrium conditions

$$dS = 0 \quad dP = 0 \quad dH = 0. \quad (49)$$

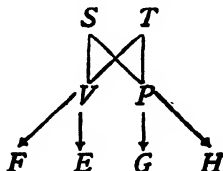
Thirdly, let us consider an infinitesimal change at constant volume and constant temperature (isothermal change). We now have, according to (44.3), the equilibrium conditions

$$dT = 0 \quad dV = 0 \quad dF = 0. \quad (50)$$

Lastly, by considering an infinitesimal change at constant pressure and constant temperature, we have, according to (47.3), the equilibrium conditions

$$dT = 0 \quad dP = 0 \quad dG = 0. \quad (51)$$

Any one of the four sets of equilibrium conditions (48), (49), (50), (51) is sufficient by itself, and has an equal claim to be regarded as fundamental. It is therefore curious that almost every text-book omits the second set (49). This omission disguises the symmetry existing between the various thermodynamic functions, represented schematically by



*Conditions of Stability.*—In order to make quite clear what is meant by stability and instability in thermodynamic systems,

we shall first discuss the significance of these expressions in a purely mechanical system. In Fig. 1 are shown in section three different equilibrium positions of a box on a stand. In positions *a* and *c* the centre of gravity *G* is lower than in any infinitely near position (consistent with the box resting on the stand), the gravitational potential energy is a minimum and the equilibrium is stable. If the position of the box be very slightly disturbed, it will of itself return to its former position. In position *b*, on the other hand, the centre of gravity *G* is higher than in any infinitely near position (consistent with the box resting on the stand), the gravitational potential energy is a maximum and the equilibrium is unstable. If the position of the box be very slightly disturbed, it will of itself move right away from its original position, and finally settle in some state of stable equilibrium such as *a* or *c*. As maxima and minima of the potential energy must alternate, so must positions of stable and of unstable equilibrium. In practice only stable equilibria are usually

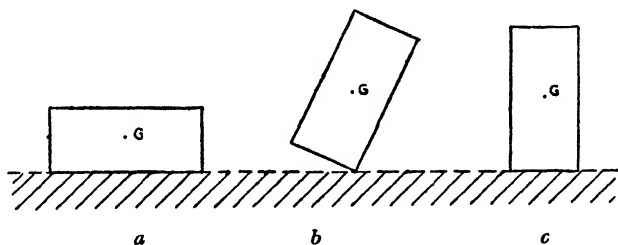


FIG. 1.

realisable, as the realisation of an unstable equilibrium requires the complete absence of any possible disturbing factors.

Whereas positions *a* and *c* are both stable, one may describe *a* as "more stable than *c*". Or one may say that *a* is "absolutely stable," while *c* is "unstable compared to *a*". By this is meant that in position *c* the potential energy is less than in any position differing only infinitesimally from *c*, but is greater than the potential energy in position *a*.

Similarly, the equilibrium of a thermodynamic system may be "absolutely stable"; or it may be "stable" compared with all states differing only infinitesimally from the given state, but unstable compared with some other state differing finitely from the given state; finally, it may be "unstable" compared with all states differing infinitesimally from the given state. Just as in the case of purely mechanical systems, equilibria unstable in the last sense are not realisable in practice. It is customary to refer to equilibria of the second type as "metastable".

One form of the condition that an equilibrium shall be of one of the first two types and so realisable is that : For given values of  $T$  and  $V$  the value of  $F$  shall be a minimum relative to states differing infinitesimally from the given state. If for the given values of  $T$  and  $V$  the value of  $F$  is less than in any other state, the equilibrium is "absolutely stable" or in the customary terminology "stable". If, on the other hand, there exists some other state with the same values of  $T$  and  $V$  at which  $F$  has a smaller value, then the equilibrium is "unstable" relatively to the latter state.

As conditions of stability of a system, in which the temperature and pressure are uniform throughout, the following twelve are all mathematically equivalent to one another :—

$$\text{for given } S \text{ and } V \text{ that } E \text{ is a minimum,} \quad (52)$$

$$\text{for given } S \text{ and } P \text{ that } H \text{ is a minimum,} \quad (53)$$

$$\text{for given } T \text{ and } V \text{ that } F \text{ is a minimum,} \quad (54)$$

$$\text{for given } T \text{ and } P \text{ that } G \text{ is a minimum,} \quad (55)$$

$$\text{for given } E \text{ and } V \text{ that } S \text{ is a maximum,} \quad (56)$$

$$\text{for given } H \text{ and } P \text{ that } S \text{ is a maximum,} \quad (57)$$

$$\text{for given } F \text{ and } V \text{ that } T \text{ is a minimum,} \quad (58)$$

$$\text{for given } G \text{ and } P \text{ that } T \text{ is a minimum,} \quad (59)$$

$$\text{for given } E \text{ and } S \text{ that } V \text{ is a minimum,} \quad (60)$$

$$\text{for given } H \text{ and } S \text{ that } P \text{ is a maximum,} \quad (61)$$

$$\text{for given } F \text{ and } T \text{ that } V \text{ is a minimum,} \quad (62)$$

$$\text{for given } G \text{ and } T \text{ that } P \text{ is a maximum.} \quad (63)$$

Any one of these is the condition for absolute or relative stability, according as the maximum (or minimum) is absolute or relative. The mutual equivalence of the above twelve conditions follows from the relations (20), (23), (27), (29).

*Thermal Equilibrium.*—Consider an isolated system of several phases in equilibrium, and suppose an infinitesimal quantity of heat  $q$  to flow from phase  $\alpha$  to phase  $\beta$  without change in volume or composition of either phase. The condition for equilibrium is, according to (48),

$$dS = 0, \quad (64)$$

or using (16.2)

$$dS^\alpha + dS^\beta = 0, \quad (65)$$

or since the process is reversible, according to (6)

$$-\frac{q}{T^\alpha} + \frac{q}{T^\beta} = 0, \quad (66)$$

or

$$T^\alpha = T^\beta, \quad (67)$$

thus confirming the fundamental property of temperature.

If we now consider two phases,  $\alpha$  and  $\beta$  at different temperatures  $T^\alpha$  and  $T^\beta$ , there will then not be thermal equilibrium. There will be a tendency for the system to approach thermal equilibrium by a change in which an infinitesimal positive quantity of heat  $q$  flows say from phase  $\alpha$  to phase  $\beta$ . Such a change is by definition a "natural" one. We therefore have, according to (5.1) and (16.2)

$$dS^\alpha + dS^\beta > 0. \quad (68)$$

If the flow of heat from  $\alpha$  to  $\beta$  is the only irreversible process taking place, any internal change taking place in either phase being reversible, the change in the entropy of each phase will be the same as in a reversible change with the same absorption or loss of heat. We therefore have, according to (6)

$$dS^\alpha = -\frac{q}{T^\alpha}, \quad (69.1)$$

$$dS^\beta = \frac{q}{T^\beta}. \quad (69.2)$$

Combining (68) and (69), we obtain

$$-\frac{q}{T^\alpha} + \frac{q}{T^\beta} > 0. \quad (70)$$

Since, by supposition,  $q$  is positive, we deduce from (70) that

$$T^\alpha > T^\beta. \quad (71)$$

This means that, *in the absence of any other irreversible changes*, heat flows from a higher temperature to a lower one, and this process will continue until the two temperatures become equal. As a matter of fact, the direction of flow of heat is determined entirely by the temperatures, and so the restriction in italics may be omitted. If we suppose two phases,  $\alpha$  and  $\beta$ , at different temperatures  $T^\alpha$  and  $T^\beta$ , where  $T^\alpha > T^\beta$  in thermal communication while some irreversible processes are taking place within the phases  $\alpha$  and  $\beta$ , then the direction in which heat tends to flow between  $\alpha$  and  $\beta$  will be determined only by the

values of  $T^\alpha$  and  $T^\beta$ , it will in fact flow from the higher temperature  $T^\alpha$  to the lower  $T^\beta$ . But owing to the heat changes accompanying the irreversible changes in the phases  $\alpha$  and  $\beta$ , it does not follow that the temperature of the hotter phase  $\alpha$  will decrease, nor that the temperature of the colder phase  $\beta$  will increase. Such a conclusion could be drawn only in the absence of any irreversible processes other than the flow of heat.

By applying condition (70) to the case that  $T^\alpha$  and  $T^\beta$  differ only infinitesimally, we deduce as a condition of the stability of a phase that, in the absence of changes of composition or volume, absorption of heat should produce increase of temperature, or for any stable phase

$$\left(\frac{\partial S}{\partial T}\right)_{v, n_i} > 0. \quad (72)$$

*Mechanical Equilibrium.*—Consider a system of several phases in equilibrium at the temperature  $T$ . Suppose the phase  $\alpha$  to increase in volume by an amount  $\delta V$  and the phase  $\beta$  to decrease by the same amount, the temperature and volume of the whole system and the composition of each phase remaining unchanged. Then, according to (50), the condition for equilibrium is

$$dF^\alpha + dF^\beta = 0, \quad (73)$$

or using (26)

$$-P^\alpha \delta V + P^\beta \delta V = 0, \quad (74)$$

and so

$$P^\alpha = P^\beta. \quad (75)$$

That is to say that the different phases in equilibrium will all be at the same pressure.

If we now consider two phases at the same temperature  $T$  and different pressures  $P^\alpha$  and  $P^\beta$ , there will then not be pressure equilibrium. There will be a tendency for the system to approach pressure equilibrium by a change in which the volume of one phase, say  $\alpha$ , increases by  $\delta V$  and that of the other phase  $\beta$  decreases by the same amount. Such a change is by definition a "natural" one. If we keep the temperatures of both phases constant, we therefore have, according to (44.1),

$$dF^\alpha + dF^\beta < 0, \quad (76)$$

or using (26)

$$-P^\alpha \delta V + P^\beta \delta V < 0. \quad (77)$$

If we suppose  $\delta V$  to be positive, it follows that

$$P^\alpha > P^\beta. \quad (78)$$

That is to say, that the phase  $\alpha$  with the greater pressure  $P^\alpha$  will increase in volume at the expense of the phase  $\beta$  with the smaller pressure. This process will tend to continue until the pressures become equal.

By applying (77) to the limiting case that the two phases  $\alpha$  and  $\beta$  are of identical composition, and that the two pressures  $P^\alpha$  and  $P^\beta$  differ only infinitesimally, we deduce that the pressure and volume of a stable phase change in opposite directions. That is to say

$$\left(\frac{\partial P}{\partial V}\right)_{T, n_i} < 0. \quad (79)$$

Any phase in which this condition is not satisfied will tend to split into two phases, the relation between  $P$  and  $V$  being different in the two phases.

*Chemical Equilibrium between Phases* ("Heterogeneous Chemical Equilibrium").—Consider a system of several phases in equilibrium at the temperature  $T$ . Suppose a small quantity  $\delta n_i$  of the species  $i$  to pass from the phase  $\alpha$  to the phase  $\beta$ , the temperature of the whole system and the pressures of the various phases being kept unchanged. Then the condition of equilibrium is according to (51)

$$dG^\alpha + dG^\beta = 0, \quad (80)$$

or using (28)

$$- \mu_i^\alpha \delta n_i + \mu_i^\beta \delta n_i = 0, \quad (81)$$

or

$$\mu_i^\alpha = \mu_i^\beta. \quad (82)$$

Thus the condition that the two phases  $\alpha$  and  $\beta$  should be in equilibrium as regards the species  $i$  is that the chemical potential  $\mu_i$  of  $i$  should have the same value in both phases.

If the chemical potential  $\mu_i^\alpha$  of  $i$  in the phase  $\alpha$  is not equal to its chemical potential  $\mu_i^\beta$  in the phase  $\beta$ , then there will be a tendency for the species  $i$  to pass from the one phase, say  $\alpha$ , to the other phase  $\beta$ . Such a change towards equilibrium is by definition a "natural" process. If we allow this change to proceed at constant temperature and pressure we have, according to (47.1)

$$dG^\alpha + dG^\beta < 0. \quad (83)$$

If we suppose the small quantity  $\delta n_i$  of  $i$  to pass from phase  $\alpha$  to phase  $\beta$ , we have, according to (28) and (83)

$$- \mu_i^\alpha \delta n_i + \mu_i^\beta \delta n_i < 0. \quad (84)$$

If we suppose  $\delta n_i$  to be positive, it follows that

$$\mu_i^\alpha > \mu_i^\beta. \quad (85)$$

That is to say, the species  $i$  tends to pass from the phase where it has the higher chemical potential to the phase where it has the lower chemical potential. The name "chemical potential," due to Willard Gibbs, was chosen to emphasise this property. The expression "escaping tendency," due to G. N. Lewis, expresses the same property.

By considering the limiting case of two phases of the same temperature and pressure and differing in composition infinitesimally as regards the species  $i$  only, we can deduce that the chemical potential of the species  $\mu_i$  in any stable phase is always increased by addition of the species  $i$ . For, suppose the two phases to be of equal quantity and composition except that  $\alpha$  contains a positive quantity  $\delta n_i$  of  $i$  more than  $\beta$ . Then the condition that  $i$  should pass from  $\alpha$  to  $\beta$  is according to (85)

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{T, P, n_j} \delta n_i > 0, \quad (86)$$

or since, by supposition,  $\delta n_i$  is positive

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{T, P, n_j} > 0. \quad (87)$$

If this condition is fulfilled, the two phases will coalesce to form a single stable phase. If, on the other hand,

$$\left(\frac{\partial \mu_i}{\partial n_i}\right)_{T, P, n_j} < 0, \quad (88)$$

the species  $i$  will tend to pass from  $\beta$  to  $\alpha$ . That is to say, a phase of the initial composition would be unstable, and would tend to split into two phases with a finite difference of composition.

The chemical potential of some other species  $j$  may be either increased or decreased by the addition of the species  $i$ . But from the Gibbs-Duhem relation (33)

$$n_i \frac{\partial \mu_i}{\partial n_i} + \sum_j n_j \frac{\partial \mu_j}{\partial n_i} = 0, \quad (89)$$

it follows that at least one of the quantities  $\frac{\partial \mu_j}{\partial n_i}$  must be negative.

*Membrane Equilibrium.*—It is to be observed that as long as a system is in "thermal" equilibrium, that is all phases are at the same temperature  $T$ , the conditions of chemical equilibrium for the various species are independent of one another and of the conditions for pressure equilibrium. If, then, two phases  $\alpha$  and  $\beta$

are separated by a fixed wall permeable to some components  $i$ , but not to other components  $k$ , the conditions that the two phases are in equilibrium as regards  $i$  is still

$$\mu_i^\alpha = \mu_i^\beta, \quad (90)$$

but in this case in general

$$P^\alpha \neq P^\beta \quad \mu_k^\alpha \neq \mu_k^\beta. \quad (91)$$

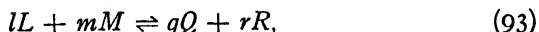
Such a partial equilibrium is called a "membrane" equilibrium.

*Systems not in Chemical Equilibrium.*—Owing to the slowness of attainment of some chemical equilibria compared with others, it is possible for a phase  $\alpha$  not in complete chemical equilibrium to remain effectively unaltered during a time in which it is able to come to equilibrium as regards the species  $i$  with some other phase  $\beta$ . When this stage is reached, we have

$$\mu_i^\alpha = \mu_i^\beta, \quad (92)$$

and in this way  $\mu_i^\alpha$  may be determinable, although the phase is not in equilibrium. For example, the attainment of equilibrium between a solution and the vapour phase as regards a volatile constituent is often rapid compared with the rate of a chemical reaction in the solution; hence, while the chemical reaction is taking place slowly, the chemical potential of a reactant may be determined at any time by measurement of its chemical potential in the vapour phase. (We shall see later that this means merely an analysis of the vapour and measurement of its pressure.)

*Chemical Equilibrium in One Phase ("Homogeneous Chemical Equilibrium").*—Suppose that in a system of one phase it is possible for some of the species to react chemically according to the scheme



where  $L, M, Q, R$  represent chemical species, and  $l, m, q, r$  are small integers determining the proportions in which they react. Imagine the reaction to proceed from left to right at constant temperature and constant pressure to an extent corresponding to

$$\epsilon lL + \epsilon mM \rightarrow \epsilon qQ + \epsilon rR, \quad (94)$$

where  $\epsilon$  is an infinitesimal number. Then, according to (51), the condition of equilibrium is

$$dG = 0, \quad (95)$$

or using (28)

$$\epsilon l\mu_L + \epsilon m\mu_M = \epsilon q\mu_Q + \epsilon r\mu_R, \quad (96)$$

or

$$l\mu_L + m\mu_M = q\mu_Q + r\mu_R. \quad (97)$$



It is to be observed that the condition for equilibrium is obtained from the formula of reaction (93) by replacing the symbol denoting each species  $i$  by that of the corresponding chemical potential  $\mu_i$ .

*Mole Fractions.*—As already mentioned, the chemical content of a phase is described by the number of moles of each species. These quantities are capacity factors (extensive properties), being additive for phases identical in state but of varying quantity. As the fundamental properties of a phase depend only on its relative composition and not on its quantity, it is convenient to introduce quantities to measure the relative composition. Such quantities are the mole-fractions  $N_i$  defined by

$$N_i = \frac{n_i}{\sum_k n_k}. \quad (98)$$

The mole fractions are intensity factors (intensive properties) being the same in two phases of the same nature but of different quantity. In a phase of  $c$  independent components, only  $c - 1$  of the mole fractions are mutually independent, because there is the identical relation

$$\sum_i N_i = 1. \quad (99)$$

*Phase Rule.*—Consider a system in complete equilibrium consisting of  $p$  phases and  $c$  independent components (by "independent" is meant just sufficient in number to define the composition of any phase). Then the system is completely defined by the quantities

$$T, P, n_i^\alpha, \quad (100)$$

in number  $(pc + 2)$ . If, however, we disregard mere variations in the quantities of the various phases, the nature of the system is adequately described by the quantities

$$T, P, N_i^\alpha, \quad (101)$$

where the mole fraction  $N_i^\alpha$  of  $i$  in the phase  $\alpha$  is, according to (98), defined by

$$N_i^\alpha = \frac{n_i^\alpha}{\sum_k n_k^\alpha}. \quad (102)$$

There are again  $(pc + 2)$  of these quantities, but as the  $N_i^\alpha$  are subject to the  $p$  identical relations

$$\sum_i N_i^\alpha = 1, \quad (103)$$

of these quantities only  $p(c - 1) + 2$  are mutually independent. Now, since the system is in complete equilibrium, we have for each component  $i$  the conditions

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots \quad (104)$$

$p - 1$  in number, or  $c(p - 1)$  such conditions in all. Hence, the number of "degrees of freedom,"  $f$  of the system or the number of independent variations of its nature, apart from mere alterations of the amounts of the various phases, consistent with maintenance of equilibrium is given by

$$f = \{p(c - 1) + 2\} - \{c(p - 1)\}, \quad (105)$$

or

$$f = c - p + 2. \quad (106)$$

This is known as the "phase rule" of Willard Gibbs.

The number 2 occurring in (106) is really incidental, and comes from our assumption that the state of a phase of given composition is completely determined by two intensity factors  $T$  and  $P$ . If, as for systems consisting only of condensed phases at not too high pressures, the pressure is irrelevant and we regard the state of a phase of given composition as sufficiently defined by its temperature, then for such systems the phase rule has the form

$$f = c - p + 1. \quad (107)$$

On the other hand, if we may not neglect the variations of state depending on, for instance, gravitational energy, the numerical term is correspondingly increased by the number of such extra independent forms of energy. Such effects are discussed in later chapters.

If the occurrence of certain components is excluded *a priori* from certain phases, the number of mole fractions  $N_i^\alpha$  required to describe these phases is reduced, but there is an equal reduction in the number of equilibrium conditions of the form (104). So the form (107) of the phase rule is unaffected.

For systems in partial equilibrium (osmotic equilibrium) the variables must be taken as  $T$ ,  $P^\alpha$ ,  $N_i^\alpha$ , being  $p(c + 1) + 1$  in number, between which there are the  $p$  identical relations

$$\sum_i N_i^\alpha = 1. \quad (108)$$

In addition we have a certain number  $r_1$  not greater than  $(p - 1)$  relations of the form

$$P^\alpha = P^\beta = P^\gamma = \dots \quad (109)$$

between phases not separated by partially impermeable membranes, and a certain number  $r_2$  not greater than  $c(p - 1)$  of the form

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\gamma = \dots \quad (110)$$

for the species in complete or osmotic equilibrium between various pairs of phases. The number of degrees of freedom  $f$  is then given by

$$f = \{p(c + 1) + 1\} - p - r_1 - r_2, \quad (111)$$

or

$$f = pc + 1 - (r_1 + r_2), \quad (112)$$

and is easily computed in any particular case. In every case we have

$$r_1 + r_2 \leq (c + 1)(p - 1). \quad (113)$$

It follows that

$$f \geq (pc + 1) - (c + 1)(p - 1), \quad (114)$$

or

$$f \geq c - p + 2, \quad (115)$$

with a minimum value  $f_{\min}$  given by

$$f_{\min} = c - p + 2, \quad (116)$$

when there is complete equilibrium throughout the system.

## NOTES AND REFERENCES

*First and Second Laws of Thermodynamics.*—A thorough discussion of the exact significance and formulation of the first and second laws of thermodynamics is given in Planck's "Treatise on Thermodynamics" and in Trevor's "General Theory of Thermodynamics."

*Notation.*—The notation used by various authors for the four characteristic functions is as follows:—

<i>Present Notation.</i>	<i>E.</i>	<i>H.</i>	<i>F.</i>	<i>G.</i>
Gibbs (Collected Works) . . . . .	$\epsilon$	$\chi$	$\psi$	$\zeta$
Massieu (C.R. 69, 858, 1087 (1869)) . . . . .	$U$	$U'$	$-t\psi$	$-t\psi'$
Duhem (Thermodynamique et Chimie) . . . . .	$U$		$F$	$\Phi$
Planck (Vorlesungen über Thermodynamik, 6th edition) . . . . .	$U$		$F$	$\Phi$
„ (English translation) . . . . .	$U$		$F$	$-t\Psi$
Lorentz (Lectures on Theoretical Physics) . . . . .	$\epsilon$		$\Psi$	$\zeta$
Fowler (Statistical Mechanics) . . . . .	$E$	$H$	$-T\Psi$	$-T\Phi$
Lewis and Randall (Thermodynamics) . . . . .	$E$	$H$	$A$	$F$
Schottky, Ulich and Wagner (Thermodynamik) . . . . .	$U$	$H$	$F$	$G$
Partington (Chemical Thermodynamics) . . . . .	$U$	$H$	$F$	$Z$

It will be observed that our notation is a compromise between that of Lewis and Randall on the one hand and that of Schottky, Ulich and Wagner on the other. We have followed the latter in using  $F$ , the initial letter of "free energy," for the function originally given that name by Helmholtz and  $G$  the initial letter of "Gibbs" to the function whose importance was first emphasised by Gibbs, and to which the name "free energy" has been assigned only by later writers. In conformity with usual practice, when the English language is used, we employ the letter  $E$  for the total energy. The four characteristic functions are in our notation thus represented by the four consecutive letters of the alphabet,  $E, F, G, H$ . The letter  $A$  is reserved to denote a surface area, a notation used by Adam.

For the "chemical potential" we have retained the name and the symbol  $\mu_i$  originally assigned to it by Gibbs. We consider the custom introduced by Lewis and Randall of replacing it by another name and symbol to emphasise the relation

$$\mu_i = \left( \frac{\partial G}{\partial n_i} \right)_{T, P, n_j},$$

is regrettable. This relation is of the same type as the relation

$$T = \left( \frac{\partial E}{\partial S} \right)_{V, n_i},$$

but no one would suggest abolishing the word "temperature" and substituting

$$\left( \frac{\partial E}{\partial S} \right)_{V, n_i}$$

throughout for the symbol  $T$ .

*Fundamental Thermodynamic Quantities and Characteristic Functions.*—For a discussion of which of the thermodynamic functions may be chosen as the fundamental ones in terms of which the others may be simply defined, see Gibbs, "Collected Works," p. 88. A condensed summary of Gibbs' thermodynamic treatment of equilibria, with numerous references, is given by Lash Miller in *Chem. Rev.* **1**, 293 (1925). A much briefer and more popular review is given by Donnan in the *J. Franklin Inst.* (Report of Centenary Celebration) (1924).

*General Conditions of Equilibrium and Stability.*—These are very thoroughly discussed in the text-book "Thermodynamik" by Schottky, Ulich and Wagner. The original source is, of course, Gibbs, but his discussion is difficult reading. A clear exposition of Gibbs' graphical treatment of stability, with experimental examples, is given by van Rijn van Alkemade in *Z. Physikal. Chem.* **11**, 289 (1893).

*Phase Rule.*—The standard work on the Phase Rule is Roozeboom's "Die Heterogene Gleichgewichte." There are several excellent shorter books on the subject, amongst which one by Rivett and one by Findlay.

## CHAPTER II

### THERMODYNAMIC RELATIONS OF GENERAL VALIDITY

*Partial Molar and Mean Molar Quantities.*—If  $J$  denotes any capacity factor of a phase, for instance any one of the quantities  $S^\alpha$ ,  $V^\alpha$ ,  $E^\alpha$ ,  $H^\alpha$ ,  $F^\alpha$  or  $G^\alpha$ , then the quantities

$$J_i = \left( \frac{\partial J}{\partial n_i} \right)_{T, P, n_j}, \quad (117)$$

are called the corresponding "partial molar" quantities. We have

$$dJ = \left( \frac{\partial J}{\partial T} \right)_{P, n_i} dT + \left( \frac{\partial J}{\partial P} \right)_{T, n_i} dP + \sum_i J_i dn_i. \quad (118)$$

Integrating this for constant  $T$ ,  $P$  and constant relative composition we obtain

$$J = \sum_i n_i J_i. \quad (119)$$

Differentiating (119) and comparing with (118) we have

$$\left( \frac{\partial J}{\partial T} \right)_{P, n_i} dT + \left( \frac{\partial J}{\partial P} \right)_{T, n_i} dP - \sum_i n_i dJ_i = 0. \quad (120)$$

As an important particular case we have

$$dT = 0 \quad dP = 0 \quad \sum_i n_i dJ_i = 0. \quad (121)$$

This gives a relation between the changes with composition of the partial molar quantities  $J_i$  of the various components at constant temperature and pressure.

In these formulæ  $J$  may represent any one of the capacity factors  $S$ ,  $V$ ,  $E$ ,  $H$ ,  $F$ ,  $G$ , and  $J_i$  is then the corresponding partial molar quantity  $S_i$ ,  $V_i$ ,  $E_i$ ,  $H_i$ ,  $F_i$ ,  $G_i$ . We have already had a special case of these relations when  $J$  represents the Gibbs free energy  $G$ , in which case according to (28) the corresponding partial molar quantity  $G_i$  is equal to  $\mu_i$ . In this case the formulæ (117), (118), (119), (120), (121) become respectively (29.3), (28), (31), (32), (33). Owing to this relation the chemical potentials are also known as the "partial molar Gibbs free energies." This

name, however, focusses attention on what is merely an incidental property of these quantities. To their fundamental property, that of determining the direction of a chemical change, corresponds the name "chemical potential" introduced by Gibbs.

The quantity  $J$  defined by

$$J = \frac{J}{\sum_i n_i}, \quad (122)$$

may be called the "mean molar" quantity.

The partial molar quantities  $J_i$  and the mean molar quantity  $J$  are intensity factors (intensive properties), since their values are for phases in a given state independent of the quantity of the phase. The partial molar quantities  $J_i$  and the mean molar quantity  $J$  are related by the formula

$$J = \sum_i N_i J_i, \quad (123)$$

derived directly from (119) and (122).

In the simplest possible case of a phase of a single component there is no difference between the partial molar quantity  $J_i$  and the mean molar quantity  $J$ . One may therefore in this case omit the epithets "partial" and "mean" and refer simply to the "molar" quantity.

In the next simplest case of a phase of two components 1 and 2, the relations between the partial molar quantities  $J_1$  and  $J_2$ , and the mean molar quantity  $J$ , can be expressed in a somewhat different form in terms of the mole fractions  $N_1$  and  $N_2$ . The relation (123) now becomes simply

$$J = N_1 J_1 + N_2 J_2. \quad (124)$$

Since  $N_1$  and  $N_2$  are subject to the identity

$$N_1 + N_2 = 1, \quad (125)$$

either one of them is sufficient to define the relative composition of the phase. We may regard  $J$ ,  $J_1$ ,  $J_2$  as functions of either  $N_1$  or of  $N_2$ , but not of both. Now consider a phase containing  $N_1$  moles of the species 1 and  $N_2$  of the species 2, that is altogether just one mole. Suppose we alter its composition infinitesimally at constant temperature and pressure, keeping the total number of moles unity, by removing  $dn$  moles of the species 1 and adding  $dn$  moles of species 2. For this infinitesimal change we have

$$-dn_1 = dn_2 = dn, \quad (126)$$

and according to (118)

$$dJ = dJ = -J_1 dn + J_2 dn. \quad (127)$$

It follows from (126) and (127) that

$$-\frac{dJ}{dN_1} = \frac{dJ}{dN_2} = -J_1 + J_2. \quad (128)$$

The relations (124) and (128) are shown graphically in Fig. 2. The abscissæ represent  $N_1$  decreasing from  $O$  to  $O'$  and  $N_2$  increasing from  $O$  to  $O'$ .

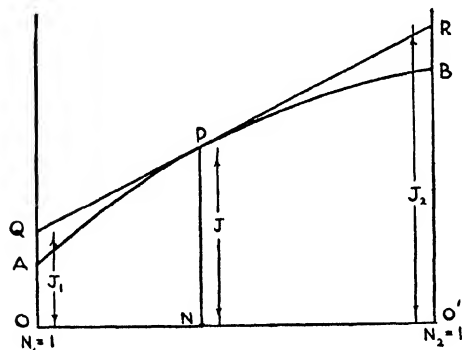


FIG. 2.

Suppose the curve  $APB$  to be a plot of the mean molar quantity  $J$  as ordinate and  $P$  to be any point on it. Let the tangent  $QPR$  to this curve at  $P$  cut the  $O$  and  $O'$  ordinates at  $Q$  and  $R$ . The partial molar quantities  $J_1$  and  $J_2$  corresponding to the composition at  $P$  are then represented respectively by the lengths  $OQ$  and  $O'R$ .

For let the ordinate through  $P$  cut  $OO'$  at  $N$ . Then the length  $ON$  is  $N_2$ , the length  $NO'$  is  $N_1$  and  $OO'$  is unity. The co-linearity of  $QPR$  is therefore expressed by

$$J = NP = N_1 \cdot OQ + N_2 \cdot O'R \quad (129)$$

and the gradient of  $QPR$  being equal to that of the curve is expressed by

$$-\frac{dJ}{dN_1} = \frac{dJ}{dN_2} = O'R - OQ. \quad (130)$$

It is clear that (129) and (130) can agree with (124) and (128) only if

$$J_1 = OQ, \quad (131.1)$$

$$J_2 = O'R. \quad (131.2)$$

In the case of three components a similar graphical construction holds, but in three dimensional space. We plot the mole-fraction composition by means of triangular co-ordinates, the three pure components being represented by the vertices  $O_1, O_2, O_3$  of an equilateral triangle. At each point within this triangle is erected a vertical straight line of length equal to the value of  $J$  for the corresponding composition. The value of  $J$  as a function of the composition is thus represented by a surface.

The tangent plane at each point  $P$  of this surface then cuts the vertical straight lines through  $O_1, O_2, O_3$  at heights equal to the values of  $J_1, J_2, J_3$  respectively.

*Heat Capacities.*—If a system of given composition be heated from the temperature  $T$  to  $T + dT$  the heat  $q$  absorbed will evidently be proportional to  $dT$ . We therefore write

$$q = CdT, \quad (132)$$

where  $C$  is independent of  $dT$ . Provided all changes taking place during the heating process are reversible, we may, according to (6), substitute

$$q = TdS, \quad (133)$$

and so obtain

$$TdS = CdT. \quad (134)$$

$C$  is then called the "heat capacity" of the system. The value of  $C$  is still not completely determined by this definition, but depends on how the volume and pressure of the system vary during the heating process. Substituting from (134) into (20.4) or (22), and remembering in either case that we are assuming the composition of the system kept constant, we obtain respectively

$$dE + PdV = CdT, \quad (135)$$

$$dH - VdP = CdT. \quad (136)$$

As an important special case we may suppose the volume of the system held constant during the heating. The constant  $C$  is then called the "heat capacity at constant volume" and is denoted by  $C_v$ . We then have, according to (134),

$$dV = 0 \quad TdS = C_v dT, \quad (137)$$

or

$$C_v = T \left( \frac{\partial S}{\partial T} \right)_{v, n_i}. \quad (138)$$

We also have, according to (135),

$$dV = 0 \quad dE = C_v dT, \quad (139)$$

or

$$C_v = \left( \frac{\partial E}{\partial T} \right)_{v, n_i}. \quad (140)$$

Either (138) or (140) may be taken as the formal definition of  $C_v$ .

As a second important case let us suppose the pressure of the system kept constant during the heating process. The constant



$C$  is then called the "heat capacity at constant pressure" and is denoted by  $C_P$ . We then have, according to (134),

$$dP = 0 \quad TdS = C_P dT, \quad (141)$$

or

$$C_P = T \left( \frac{\partial S}{\partial T} \right)_{P, n_i}, \quad (142)$$

while according to (136) we have

$$dP = 0 \quad dH = C_P dT, \quad (143)$$

or

$$C_P = \left( \frac{\partial H}{\partial T} \right)_{P, n_i}. \quad (144)$$

Either (142) or (144) may be regarded as the formal definition of  $C_P$ .

*Partial and Mean Molar Heat Capacities.*—From the heat capacities  $C_V$  and  $C_P$  we derive the corresponding partial molar heat capacities  $C_{V_i}$  and  $C_{P_i}$  and mean molar heat capacities  $\bar{C}_V$  and  $\bar{C}_P$ . These are defined by

$$C_{V_i} = \left( \frac{\partial C_V}{\partial n_i} \right)_{T, P, n_j} = \left( \frac{\partial E_i}{\partial T} \right)_{V, n_i, n_j} = T \left( \frac{\partial S_i}{\partial T} \right)_{V, n_i, n_j}, \quad (145)$$

$$C_{P_i} = \left( \frac{\partial C_P}{\partial n_i} \right)_{T, P, n_j} = \left( \frac{\partial H_i}{\partial T} \right)_{P, n_i, n_j} = T \left( \frac{\partial S_i}{\partial T} \right)_{P, n_i, n_j}, \quad (146)$$

$$\bar{C}_V = \frac{C_V}{\sum_i n_i} = \left( \frac{\partial E}{\partial T} \right)_{V, n_i, n_j} = T \left( \frac{\partial S}{\partial T} \right)_{V, n_i, n_j}, \quad (147)$$

$$\bar{C}_P = \frac{C_P}{\sum_i n_i} = \left( \frac{\partial H}{\partial T} \right)_{P, n_i, n_j} = T \left( \frac{\partial S}{\partial T} \right)_{P, n_i, n_j}. \quad (148)$$

The relations between the various partial molar heat capacities at constant volume or pressure and the corresponding mean molar heat capacity are of the same form as for any other partial molar and mean molar quantities. One has merely to write  $C_V$  or  $C_P$  for  $J$ ,  $C_{V_i}$  or  $C_{P_i}$  for  $J_i$  and  $C_V$  or  $C_P$  for  $J$  in any of the relations.

For convenience of notation we may sometimes abbreviate  $C_{P_i}$  to  $C_i$  but  $C_{V_i}$  will always be written in full.

*Relations between Differential Coefficients.*—Formulæ (20), (23), (27), (29) give the most important differential coefficients of  $E$ ,  $H$ ,  $F$ ,  $G$  with respect to  $S$ ,  $T$ ,  $V$ ,  $P$ ,  $n_i$ . Further relations

between various partial differential coefficients may be obtained from these by use of the mathematical identity

$$\frac{\partial}{\partial x} \left( \frac{\partial f}{\partial y} \right) = \frac{\partial}{\partial y} \left( \frac{\partial f}{\partial x} \right). \quad (149)$$

As important examples we may mention the following :—

$$f = F \quad x = V \quad y = T \quad \text{gives} \quad \left( \frac{\partial S}{\partial V} \right)_{T, n_i} = \left( \frac{\partial P}{\partial T} \right)_{V, n_i}, \quad (150)$$

$$f = G \quad x = P \quad y = T \quad \text{gives} \quad \left( \frac{\partial S}{\partial P} \right)_{T, n_i} = - \left( \frac{\partial V}{\partial T} \right)_{P, n_i}, \quad (151)$$

$$f = G \quad x = T \quad y = n_i \quad \text{gives} \quad \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_i} = - \left( \frac{\partial S}{\partial n_i} \right)_{T, P, n_j} = -S_i, \quad (152)$$

$$f = G \quad x = P \quad y = n_i \quad \text{gives} \quad \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_i} = \left( \frac{\partial V}{\partial n_i} \right)_{T, P, n_j} = V_i. \quad (153)$$

*Volume Derivative of Energy and Pressure Coefficient of Heat Content.*—The isothermal volume derivative of the energy is obtained by differentiating formula (24)

$$F = E - TS, \quad (154)$$

with respect to the volume keeping the temperature and composition constant. Using (27.2) and (150), we obtain

$$-P = \left( \frac{\partial E}{\partial V} \right)_{T, n_i} - T \left( \frac{\partial P}{\partial T} \right)_{V, n_i}, \quad (155.1)$$

or

$$\left( \frac{\partial E}{\partial V} \right)_{T, n_i} = T \left( \frac{\partial P}{\partial T} \right)_{V, n_i} - P. \quad (155.2)$$

Similarly, to obtain the isothermal pressure derivative of the heat content, we differentiate formula (25)

$$G = H - TS, \quad (156)$$

with respect to the pressure keeping the temperature and composition constant. Using (29.2) and (151), we obtain

$$V = \left( \frac{\partial H}{\partial P} \right)_{T, n_i} + T \left( \frac{\partial V}{\partial T} \right)_{P, n_i}, \quad (157.1)$$

or

$$\left( \frac{\partial H}{\partial P} \right)_{T, n_i} = -T \left( \frac{\partial V}{\partial T} \right)_{P, n_i} + V, \quad (157.2)$$

*Further Relation between Differential Coefficients.*—Another mathematical identity sometimes required is

$$\left(\frac{\partial x}{\partial y}\right)_z = - \left(\frac{\partial z}{\partial y}\right)_x \bigg/ \left(\frac{\partial z}{\partial x}\right)_y = - \left(\frac{\partial x}{\partial z}\right)_y \bigg/ \left(\frac{\partial y}{\partial z}\right)_x. \quad (158)$$

It is useful for obtaining differential coefficients in which the function kept constant is one that is generally regarded as a dependent variable. We give two examples that we shall use later. Firstly, we have

$$\begin{aligned} \left(\frac{\partial T}{\partial V}\right)_E &= - \left(\frac{\partial E}{\partial V}\right)_T \bigg/ \left(\frac{\partial E}{\partial T}\right)_V \\ &= \frac{P - T\left(\frac{\partial P}{\partial T}\right)_V}{C_V}, \end{aligned} \quad (159)$$

using (155.2) and (140). Secondly, we have

$$\begin{aligned} \left(\frac{\partial T}{\partial P}\right)_H &= - \left(\frac{\partial H}{\partial P}\right)_T \bigg/ \left(\frac{\partial H}{\partial T}\right)_P \\ &= \frac{-V + T\left(\frac{\partial V}{\partial T}\right)_P}{C_P}, \end{aligned} \quad (160)$$

using (157.2) and (144).

*Relation between Heat Capacities.*—A relation between  $C_P$  and  $C_V$  may be obtained as follows. By the definitions (144) and (140)

$$\begin{aligned} C_P - C_V &= \left(\frac{\partial H}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \\ &= \left(\frac{\partial E}{\partial T}\right)_P + \left(\frac{\partial PV}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \\ &= \left(\frac{\partial E}{\partial T}\right)_V + \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial V}{\partial T}\right)_P + P\left(\frac{\partial V}{\partial T}\right)_P - \left(\frac{\partial E}{\partial T}\right)_V \\ &= T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P, \end{aligned} \quad (161)$$

using (155.2).

By differentiating (161) with respect to  $n_i$  we obtain the analogous relation between the partial molar heat capacities

$$C_{P_i} - C_{V_i} = T\left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V_i}{\partial T}\right)_P. \quad (162)$$

Similarly, by dividing (161) by  $\sum_i n_i$  we obtain the analogous

relation between the mean molar heat capacities

$$C_P - C_V = T \left( \frac{\partial P}{\partial T} \right)_V \left( \frac{\partial V}{\partial T} \right)_P. \quad (163)$$

*Gibbs-Helmholtz Formulæ.*—By eliminating  $S$  from (24) and (27.1) we obtain

$$F - T \left( \frac{\partial F}{\partial T} \right)_V = E. \quad (164)$$

Similarly, from (25) and (29.1) we obtain

$$G - T \left( \frac{\partial G}{\partial T} \right)_P = H. \quad (165)$$

These formulæ may also be written in the forms

$$\left( \frac{\partial F/T}{\partial T} \right)_V = - \frac{E}{T^2} \quad (166)$$

and

$$\left( \frac{\partial G/T}{\partial T} \right)_P = - \frac{H}{T^2}. \quad (167)$$

Other more important relations are directly derivable from the above relations. Thus, by applying (164) or (166) to the initial and final states of an isothermal process at given constant pressure, and subtracting the first from the second, we obtain

$$\Delta F - T \left( \frac{\partial \Delta F}{\partial T} \right)_V = \Delta E, \quad (168)$$

$$\left( \frac{\partial \Delta F/T}{\partial T} \right)_V = - \frac{\Delta E}{T^2}. \quad (169)$$

Similarly, by applying (165) or (167) to the initial and final states of an isothermal process at given constant volume, and subtracting the first from the second, we obtain

$$\Delta G - T \left( \frac{\partial \Delta G}{\partial T} \right)_P = \Delta H, \quad (170)$$

$$\left( \frac{\partial \Delta G/T}{\partial T} \right)_P = - \frac{\Delta H}{T^2}. \quad (171)$$

Formula (170) or (171) is known as the Gibbs-Helmholtz relation. More loosely this name is assigned to any of the relations (164), (165), (166), (167), (168), (169).

*Differential Relations between Partial Molar Quantities.*—Given

any differential relation homogeneous of first degree in capacity factors, it is clear that one can always obtain a corresponding relation between partial molar quantities by differentiating with respect to  $n_i$ , keeping  $T$  and  $P$  constant. For example, from (161) we derived (162).

Most important of such relations are those derived from (165) and (167), namely

$$\mu_i - T \left( \frac{\partial \mu_i}{\partial T} \right)_{P, n_i, n_j} = H_i, \quad (172)$$

and

$$\left( \frac{\partial \mu_i / T}{\partial T} \right)_{P, n_i, n_j} = - \frac{H_i}{T^2}. \quad (173)$$

*Heats of Reaction.*—Suppose a system to undergo a finite isothermal change, and let the operator  $\Delta$  denote the excess of a final over an initial value. The heat absorbed during this process will be called the heat of reaction. For a process at constant volume, since no work is performed, we have for the heat of reaction  $L_V$

$$L_V = \Delta E. \quad (174)$$

For a process occurring at constant pressure the work performed on the system is  $-P\Delta V$ , and so the heat of reaction  $L_P$  is given by

$$L_P = \Delta E + \Delta(PV) = \Delta H. \quad (175)$$

For convenience of notation we shall write simply  $L$  instead of  $L_P$  to facilitate the use of other suffices, but  $L_V$  will never be abbreviated.

It is to be observed that we have conventionally chosen the sign of the heat of reaction to be positive when heat is absorbed in the process mentioned. This is in agreement with common usage in the expressions "heat of fusion" and "heat of evaporation." The custom of using other similar expressions, some to denote heat absorbed, others to denote heat emitted, is to be deplored.

*Kirchhoff's Formulae.*—Suppose a system at the temperature  $T$  to undergo some finite change defined by the initial and final values of the  $V^\alpha$  and  $n_i^\alpha$  of each phase  $\alpha$  and each species  $i$ . Then we have the mathematical identity

$$\frac{\partial}{\partial T} \Delta E = \Delta \frac{\partial E}{\partial T} = \Delta C_V. \quad (176)$$

In the important case that the initial and final values of  $\sum_{\alpha} V^{\alpha}$  or  $V$  are equal, this becomes

$$\frac{\partial L_V}{\partial T} = \Delta C_V. \quad (177)$$

Similarly, for a finite change defined by the initial and final values of  $P$  and the  $n_i^{\alpha}$ , we have the identity

$$\frac{\partial}{\partial T} \Delta H = \Delta \frac{\partial H}{\partial T} = \Delta C_P. \quad (178)$$

In the important case that the final and initial values of  $P$  are identical, this becomes

$$\frac{\partial L_P}{\partial T} = \Delta C_P. \quad (179)$$

Formulæ (177) and (179) are due to Kirchhoff.

*Isothermal and Adiabatic Compressibilities.*—The effect of pressure on the volume at constant temperature is conveniently measured by the "isothermal compressibility" or more shortly the "compressibility"  $\kappa$  defined by

$$\kappa = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T. \quad (180.1)$$

Similarly, the dependence of volume on pressure under adiabatic conditions may be measured by the "adiabatic compressibility"  $\kappa_S$  defined by

$$\kappa_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_S. \quad (180.2)$$

For a system of given composition there is a relation between the adiabatic and the isothermal compressibilities. This may be derived as follows.

For the reversible adiabatic change, we have

$$dS = 0. \quad (181)$$

According to (138) and (150) we may write (181) in the form

$$\frac{C_V}{T} dT + \left( \frac{\partial P}{\partial T} \right)_V dV = 0, \quad (182)$$

and according to (142) and (151) we may write (181) in the form

$$\frac{C_P}{T} dT - \left( \frac{\partial V}{\partial T} \right)_P dP = 0. \quad (183)$$

Since (182) and (183) both refer to the same adiabatic process, we may eliminate  $dT$ , and so obtain

$$\begin{aligned} dP &= -\frac{C_P}{C_V}\left(\frac{\partial P}{\partial T}\right)_V \bigg/ \left(\frac{\partial V}{\partial T}\right)_P dV \\ &= \frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_T dV, \end{aligned} \quad (184)$$

using (158). This may be written

$$\left(\frac{\partial P}{\partial V}\right)_S = \frac{C_P}{C_V}\left(\frac{\partial P}{\partial V}\right)_T, \quad (185)$$

or

$$\kappa_S = \frac{C_V}{C_P}\kappa, \quad (186)$$

the required relation between the adiabatic and the isothermal compressibilities.

*Coefficient of Thermal Expansion.*—The effect of change of temperature on the volume is conveniently measured by the coefficient of thermal expansion  $\alpha$  defined by

$$\alpha = \frac{1}{V}\left(\frac{\partial V}{\partial T}\right)_P. \quad (187)$$

## NOTES AND REFERENCES

*Partial Molar Quantities.*—These quantities were first accurately defined and treated in detail by Lewis and Randall (Thermodynamics). They use the notation  $\bar{J}_i$ , where we use  $J_i$ ; the bar over the symbol  $J_i$  seems superfluous, and following Schottky, Ulich and Wagner (Thermodynamik) we have omitted it.

## CHAPTER III

### SYSTEMS OF ONE COMPONENT

HAVING now obtained most of the general formulæ of thermodynamics we are in a position to apply them to special systems. In the present chapter we shall confine ourselves to systems of a single component.

*One Component in One Phase.*—According to the phase rule a system of one component in one phase has two degrees of freedom. Therefore the state of a given quantity of a single component in a single phase may be defined by its temperature and its volume, or alternatively by its temperature and its pressure, or again by its pressure and its volume.

*Constant Volume Thermometry.*—Let us consider a given quantity of a single component in a single phase, and let us choose as the independent variables defining its state the pressure and the volume. Then any other property of the system may be regarded as a function of the pressure and volume. In particular for the isothermal volume derivative of the energy we may write

$$\left(\frac{\partial E}{\partial V}\right)_T = \epsilon(P, V), \quad (188.1)$$

where  $\epsilon(P, V)$  is a function of the pressure and the volume. Formula (155.2) then takes the form

$$\epsilon = -P + T\left(\frac{\partial P}{\partial T}\right)_V. \quad (188.2)$$

If, now, we consider changes at constant volume, (188.2) may be written

$$(P + \epsilon)dT = TdP, \quad (188.3)$$

or

$$d \log T = \frac{dP}{P + \epsilon}. \quad (188.4)$$

If we integrate this between given limits we obtain

$$\frac{T_2}{T_1} = \exp \left\{ \int_{P_1}^{P_2} \frac{dP}{P + \epsilon} \right\}, \quad (189)$$



where  $T_1, T_2$  are the temperatures corresponding respectively to the pressures  $P_1, P_2$ .

Formula (189) shows how any single component in a single phase may be used as a constant volume thermometer, provided we know the value of  $\epsilon$  as a function of the pressure for the given volume of the system. For the right-hand side of (189) can then be evaluated, and so the ratio of any two temperatures is determined as a function of the pressures.

*Constant Pressure Thermometry.*—Let us again consider a single component in a single phase, and again choose, as independent variables defining its state, the pressure and the volume. Then the pressure derivative of the heat content may be regarded as a function of the pressure and volume, and we accordingly write

$$\left(\frac{\partial H}{\partial P}\right)_T = \eta(P, V), \quad (190.1)$$

where  $\eta(P, V)$  denotes a function of  $P$  and  $V$ . Formula (157.2) then takes the form

$$\eta = V - T\left(\frac{\partial V}{\partial T}\right)_P. \quad (190.2)$$

If now we consider changes at constant pressure (190.2) may be written

$$(V - \eta)dT = TdV, \quad (190.3)$$

or

$$d \log T = \frac{dV}{V - \eta}. \quad (190.4)$$

If we integrate this between definite limits we obtain

$$\frac{T_2}{T_1} = \exp \left\{ \int_{V_1}^{V_2} \frac{dV}{V - \eta} \right\}, \quad (191)$$

where  $T_1, T_2$  are the temperatures corresponding to the volumes  $V_1, V_2$ .

Formula (191) shows how any single component in a single phase may be used as a constant pressure thermometer provided we know the value of  $\eta$  as a function of the volume for the given pressure of the system. For the right-hand side of (191) can then be evaluated, and so the ratio of any two temperatures is determined as a function of the volumes.

*Single Perfect Gas.*—If a single substance throughout a certain range of pressures and volumes has the special property that its energy is a function of its temperature only, then a constant

volume thermometer making use of such a substance will behave in a specially simple way. For in this case we have

$$\left(\frac{\partial E}{\partial V}\right)_T = \epsilon(P, V) = 0, \quad (192)$$

and so (189) simplifies to

$$\frac{T_2}{T_1} = \exp \left\{ \int_{P_1}^{P_2} \frac{dP}{P} \right\} = \frac{P_2}{P_1}. \quad (193)$$

That is to say, that at a given volume the absolute temperature is proportional to the pressure.

If, on the other hand, a substance has throughout a certain range of pressures and volumes, the property that its heat content is a function of the temperature only, then such a substance will behave in a specially simple way if used as a constant pressure thermometer. For such a substance we have

$$\left(\frac{\partial H}{\partial P}\right)_T = \eta(P, V) = 0, \quad (194)$$

and so (191) simplifies to

$$\frac{T_2}{T_1} = \exp \left\{ \int_{V_1}^{V_2} \frac{dV}{V} \right\} = \frac{V_2}{V_1}. \quad (195)$$

That is to say, that at a given pressure the absolute temperature is proportional to the volume.

Finally, let us consider a substance with the property that both its energy and its heat content are functions of the temperature only. A substance with this property is called a "perfect gas." For such a substance it then follows immediately from (21) that the product  $PV$  is a function of the temperature only, that is to say

$$\text{for given } T, \quad PV = \text{constant}. \quad (196\cdot1)$$

This is known as Boyle's Law for perfect gases. Further, we know by (193) that

$$\text{for given } V, \quad P \propto T, \quad (196\cdot2)$$

and by (195) that

$$\text{for given } P, \quad V \propto T. \quad (196\cdot3)$$

This last relation is known as Charles' Law for a perfect gas.

The three relations (196·1), (196·2), (196·3) may be combined into the one formula

$$PV = \lambda T, \quad (197)$$

where  $\lambda$  is a constant for the given quantity of gas.

It is customary to define a single perfect gas as a substance obeying Boyle's Law, which states that at constant temperature the volume of a given quantity of a perfect gas is inversely proportional to the pressure, and Charles' Law, which states that at given pressure the volume of a given quantity of gas is directly proportional to the absolute temperature. Thermodynamics can naturally tell us nothing as to when these laws are obeyed, only that substances obeying them will have certain other properties. Both these laws are deducible by the methods of statistical mechanics from the simplest possible assumptions concerning the molecular nature of a gas. Commencing with these laws as the definition of a perfect gas, one could by purely thermodynamic reasoning deduce amongst other things that the energy  $E$  and the heat content  $H$  of a given quantity of a perfect gas depend only on the temperature, but not on the pressure or volume. As a useful thermodynamic exercise, we have reversed the usual order and defined a single substance as a perfect gas if the energy  $E$  and the heat content  $H$  of a given quantity depend only on the temperature, but not on the pressure or volume.

Since  $T$  and  $P$  are intensity factors, while  $V$  is a capacity factor, it is clear that  $\lambda$  must be proportional to  $n$  the number of units of gas. We thus have

$$PV = nRT, \quad (198)$$

where  $R$  is independent of the quantity of gas. By suitable choice of the unit of quantity for different gases,  $R$  can be made independent of the nature of the gas, and is then called the "gas constant". The corresponding quantity of gas is called the "mole". It need hardly be mentioned that a more natural definition of the mole is obtained by reference to the molecular properties of the gas. But the definition given here is thermodynamically adequate and illustrates the fact that thermodynamic reasoning is independent of any molecular theory.

Applying (198) to a single mole of the perfect gas, we obtain

$$PV = RT, \quad (199)$$

the equation of state of a perfect gas.

Differentiating the relation (192) with respect to  $T$ , and using (149), we obtain for a perfect gas

$$\left(\frac{\partial C_V}{\partial V}\right)_T = \frac{\partial}{\partial V} \frac{\partial E}{\partial T} = \frac{\partial}{\partial T} \frac{\partial E}{\partial V} = 0. \quad (200)$$

Similarly, differentiating (194) with respect to  $T$ , and using (149), we have for a perfect gas

$$\left(\frac{\partial C_P}{\partial P}\right)_T = \frac{\partial}{\partial P} \frac{\partial H}{\partial T} = \frac{\partial}{\partial T} \frac{\partial H}{\partial P} = 0. \quad (201)$$

Thus, both the heat capacities  $C_V$  and  $C_P$  of a given quantity of perfect gas depend only on the temperature, but not the volume or pressure.

For the relation between the two heat capacities  $C_V$  and  $C_P$  we have, by (161) and (198),

$$C_P - C_V = T \left(\frac{\partial P}{\partial T}\right)_V \left(\frac{\partial V}{\partial T}\right)_P = nR, \quad (202)$$

or for the molar heat capacities  $C_V$  and  $C_P$

$$C_P - C_V = R. \quad (203)$$

For the entropy of  $n$  moles of a single perfect gas, we have, using (142) and (151),

$$\begin{aligned} dS &= \frac{C_P}{T} dT - \left(\frac{\partial V}{\partial T}\right)_P dP \\ &= n \frac{C_P}{T} dT - nR \frac{dP}{P}, \end{aligned} \quad (204)$$

using (148) and (198). Integration gives

$$S = n \int^T C_P d \log T - nR \log P. \quad (205)$$

If, as is sometimes the case,  $C_P$  is independent of the temperature as well as the pressure (this condition is not necessarily fulfilled by every perfect gas), then

$$S = nC_P \log T - nR \log P + nS^\circ. \quad (206)$$

where  $S^\circ$  is a constant depending on the conventional choice of zero entropy. By using (203) and (198) we can transform (205) to the form

$$S = n \int^T C_V d \log T + nR \log V - nR \log n, \quad (207)$$

or (206) to the form

$$S = nC_V \log T + nR \log V - nR \log n + nS^{\circ'}, \quad (208)$$

where

$$S^{\circ'} = S^\circ - R \log R. \quad (209)$$

For the energy  $E$  we have, according to (145) and (192)

$$E = n \int^T C_v dT, \quad (210)$$

and for the heat content  $H$ , according to (146) and (194)

$$H = n \int^T C_p dT. \quad (211)$$

Hence for the Helmholtz free energy  $F$  by (24), (210) and (207)

$$F = n \int^T C_v dT - nT \int^T C_v d \log T - nRT \log V + nRT \log n, \quad (212)$$

and for the Gibbs free energy  $G$  by (25), (211) and (205),

$$G = n \int^T C_p dT - nT \int^T C_p d \log T + nRT \log P. \quad (213)$$

From (27.3) and (212) we deduce for the chemical potential

$$\begin{aligned} \mu &= \left( \frac{\partial F}{\partial n} \right)_{T, v} \\ &= \int^T C_v dT - T \int^T C_v d \log T - RT \log V + RT \log n + RT. \end{aligned} \quad (214)$$

Alternatively, from (29.3) and (213) we deduce

$$\begin{aligned} \mu &= \left( \frac{\partial G}{\partial n} \right)_{T, P} \\ &= \int^T C_p dT - T \int^T C_p d \log T + RT \log P. \end{aligned} \quad (215)$$

The identity of formulæ (214) and (215), apart from an arbitrary additive constant, follows from (203) and (198). It is convenient to abbreviate (215) to the form

$$\mu = \mu^\circ(T) + RT \log P, \quad (216)$$

where  $\mu^\circ(T)$  depends only on the temperature and

$$\begin{aligned} \frac{d\mu^\circ/T}{dT} &= - \frac{1}{T^2} \int^T C_p dT \\ &= - \frac{H}{T^2} \end{aligned} \quad (217)$$

which is, according to the definition of a perfect gas, independent of the volume or pressure.

The isothermal compressibility  $\kappa$  of a perfect gas is, according to (180.1) and (199), given by

$$\kappa = - \frac{1}{V} \left( \frac{\partial V}{\partial T} \right)_P = \frac{1}{P}. \quad (218.1)$$

The adiabatic compressibility  $\kappa_s$  is, according to (186) and (218.1), given by

$$\kappa_s = \frac{C_V}{C_P} \frac{1}{P}. \quad (218.2)$$

The equation for a reversible adiabatic change of a perfect gas is, according to (185) and (198),

$$\left(\frac{\partial P}{\partial V}\right)_s = \frac{C_P}{C_V} \left(\frac{\partial P}{\partial V}\right)_T = -\gamma \frac{P}{V} \quad (219)$$

where

$$\gamma = \frac{C_P}{C_V} = \frac{C_P}{C_V}. \quad (220)$$

For perfect gases we have seen that  $C_P$ ,  $C_V$  are at a given temperature independent of the volume or pressure. If, as is sometimes, though not necessarily always, the case, they are also independent of the temperature we can integrate (219) and obtain

$$P \propto V^{-\gamma}. \quad (221)$$

Eliminating  $V$  from (198) and (221) we have

$$P^{\gamma-1} \propto T^{\gamma}. \quad (222)$$

Finally, eliminating  $P$  from (221) and (222), we find

$$V^{\gamma-1} \propto T^{-1}. \quad (223)$$

The coefficient of thermal expansion of a perfect gas is, according to (187) and (199), given by

$$\alpha = \frac{1}{V} \left(\frac{\partial V}{\partial T}\right)_P = \frac{1}{T}. \quad (224)$$

*Joule Effect and Joule-Thomson Effect.*—In Joule's classical experiment a gas is suddenly allowed to expand adiabatically without doing any work, and the change of temperature is measured. As there is no exchange of heat with the surroundings nor any performance of work, the process takes place at constant energy and the effect is measured by  $\left(\frac{\partial T}{\partial V}\right)_E$ . But according to (159)

$$\left(\frac{\partial T}{\partial V}\right)_E = \frac{P - T \left(\frac{\partial P}{\partial T}\right)_V}{C_V}. \quad (225)$$

In the Joule-Thomson experiment a stream of gas in a thermally insulated container is forced through a plug, the pressure being greater on the near side than on the far side, and the temperature change is measured. The plug is supposed to be thermally non-conducting. When a given quantity of gas passes through the plug the work done on the gas on the near side is  $P^\alpha V^\alpha$ , and that done by the gas on the far side is  $P^\beta V^\beta$ , the indices  $\alpha$  and  $\beta$  referring to values on the near and far side of the plug. As no heat is exchanged with the surroundings we have, according to the first law of thermodynamics (2),

$$E^\alpha + P^\alpha V^\alpha = E^\beta + P^\beta V^\beta, \quad (226)$$

or according to (21)

$$H^\alpha = H^\beta. \quad (227)$$

Thus the "Joule-Thomson effect" is measured by  $\left(\frac{\partial T}{\partial P}\right)_H$ . But according to (160)

$$\left(\frac{\partial T}{\partial P}\right)_H = \frac{-V + T\left(\frac{\partial V}{\partial T}\right)_P}{C_P}. \quad (228)$$

The Joule and Joule-Thomson effects may be positive or negative depending on the temperature, pressure and nature of the gas. The variation with pressure is generally very small compared with the variation with temperature. The temperature at which either effect changes sign is called the "inversion point for that effect." For a perfect gas we have according to (198)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T}, \quad (229)$$

and

$$\left(\frac{\partial P}{\partial T}\right)_V = \frac{P}{T}. \quad (230)$$

Substituting (229) into (225) and (230) into (228) we see that for a perfect gas both effects vanish. That this must be the case may be seen still more directly from the relations of the form (158)

$$-\left(\frac{\partial T}{\partial V}\right)_E = \left(\frac{\partial E}{\partial V}\right)_T \left(\frac{\partial T}{\partial E}\right)_V, \quad (231)$$

$$-\left(\frac{\partial T}{\partial P}\right)_H = \left(\frac{\partial H}{\partial P}\right)_T \left(\frac{\partial T}{\partial H}\right)_P, \quad (232)$$

if we recall that we defined a perfect gas as a substance for which

$$\left(\frac{\partial E}{\partial V}\right)_T = 0, \quad (233.1)$$

$$\left(\frac{\partial H}{\partial P}\right)_T = 0, \quad (233.2)$$

and that the second factors  $\left(\frac{\partial T}{\partial E}\right)_V$  and  $\left(\frac{\partial T}{\partial H}\right)_P$  in (231) and (232), being the reciprocals of  $C_V$  and  $C_P$ , are finite.

*Imperfect Gases.*—For imperfect gases various equations of state have been proposed, the best-known being that of van der Waals,

$$\left(P + \frac{a}{V^2}\right)(V - b) = RT, \quad (234)$$

where  $a$  and  $b$  are constants, that of Berthelot,

$$\left(P + \frac{a'}{TV^2}\right)(V - b) = RT, \quad (235)$$

where  $a'$  and  $b$  are constants, and that of Dieterici,

$$P(V - b) = RTe^{-A/RTV}, \quad (236)$$

where  $A$  and  $b$  are constants. All these equations are semi-empirical, and valid only over a limited range of temperatures and pressures. It has been shown by Fowler by statistical mechanical considerations that the so-called "constants"  $a$  and  $b$  may for small deviations from perfection be independent of the pressure, but that they cannot be independent of the temperature.

The most convenient form of accurate equation of state of general validity for a single gas is that used by Kammerlingh-Onnes,

$$PV = RT\{1 + B \cdot P + C \cdot P^2 + D \cdot P^3 + \dots\}, \quad (237)$$

where  $B$ ,  $C$ ,  $D$ ,  $\dots$  are functions of the temperature, but not of the pressure.

For the dependence of the chemical potential  $\mu$  on the pressure at constant temperature, we have, according to (153),

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V, \quad (238)$$

or

$$\mu = \int^P V dP. \quad (239)$$



Substituting from (237) into (239), we obtain

$$\begin{aligned}\mu &= \int^P RT \left\{ \frac{1}{P} + B + C \cdot P + D \cdot P^2 + \dots \right\} dP \\ &= \mu^\circ(T) + RT \left\{ \log P + B \cdot P + \frac{1}{2} C \cdot P^2 + \frac{1}{3} D \cdot P^3 + \dots \right\}, \quad (240)\end{aligned}$$

where  $\mu^\circ(T)$  depends only on the temperature.

The compressibility is, according to (180.1) and (237), given by

$$\begin{aligned}\kappa &= -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T = -\frac{1}{V} \left( \frac{\partial V}{\partial P} \right)_T \\ &= \frac{1}{P} \cdot \frac{1 - C \cdot P^2 - 2D \cdot P^3}{1 + B \cdot P + C \cdot P^2 + D \cdot P^3 + \dots} \quad (241)\end{aligned}$$

*Fugacity and Activity Coefficient of Gas.*—The “fugacity”  $P^*$  of a single gas, a useful conception due to G. N. Lewis, is defined by the relation

$$\mu = \mu^\circ(T) + RT \log P^*, \quad (242.1)$$

where  $\mu^\circ(T)$  is a function of the temperature only, together with one of the conditions

$$\frac{P^*}{P} \rightarrow 1 \quad \text{as } P \rightarrow 0, \quad (242.2)$$

or

$$\frac{P^*V}{RT} \rightarrow 1 \quad \text{as } P \rightarrow 0, \quad (242.3)$$

these being equivalent to each other. As all gases become perfect at sufficiently low pressures, the fugacity is at low pressures identical with the pressure of the gas. At higher pressures, where the gas is no longer perfect, the ratios  $\frac{P^*}{P}$  and  $\frac{P^*V}{RT}$  deviate from unity.

Let us define quantities  $f'$  and  $f$  by the relations

$$\frac{P^*}{P} = f', \quad (243)$$

$$\frac{P^*V}{RT} = f. \quad (244)$$

Then both  $f'$  and  $f$  are unity for a perfect gas, and in general  $1 - f'$  and  $1 - f$  or  $\log f'$  and  $\log f$  are convenient measures of the deviation of the gas from perfection. Either of the quantities  $f'$  or  $f$  may be called the “activity coefficient” of the gas, but the two functions must not be confused.

In the case that the equation of state may be represented by (237), we have, according to (240) and (242),

$$\log P^* = \log P + B \cdot P + \frac{1}{2}C \cdot P^2 + \frac{1}{3}D \cdot P^3 + \dots, \quad (245)$$

and so

$$\log f' = B \cdot P + \frac{1}{2}C \cdot P^2 + \frac{1}{3}D \cdot P^3 + \dots \quad (246)$$

For  $f$  we obtain from (244), (245) and (237)

$$\begin{aligned} \log f &= \log \frac{P^*}{P} + \log \frac{PV}{RT} \\ &= \{B \cdot P + \frac{1}{2}C \cdot P^2 + \frac{1}{3}D \cdot P^3 + \dots\} \\ &\quad + \log \{1 + B \cdot P + C \cdot P^2 + D \cdot P^3 + \dots\}. \end{aligned} \quad (247)$$

*Dependence of Fugacity and of Activity Coefficient on Temperature.*—In terms of the fugacity the general formula (173),

$$\left(\frac{\partial \mu/T}{\partial T}\right)_P = -\frac{H}{T^2}, \quad (248)$$

becomes

$$\frac{d\mu^\circ/T}{dT} + R\left(\frac{\partial \log P^*}{\partial T}\right)_P = -\frac{H}{T^2}. \quad (249)$$

But in the limit of low pressures  $P^*$  becomes simply  $P$ , which is not a function of the temperature, and (249) becomes

$$\frac{d\mu^\circ/T}{dT} = -\frac{H^\circ}{T^2}, \quad (250)$$

where  $H^\circ$  is the value of  $H$  at any pressure sufficiently low for the gas to be perfect. By subtraction of (250) from (249) we obtain

$$\left(\frac{\partial \log P^*}{\partial T}\right)_P = \frac{H^\circ - H}{RT^2}. \quad (251)$$

In terms of the activity coefficient  $f'$  of the first kind (251) becomes

$$\left(\frac{\partial \log Pf'}{\partial T}\right)_P = \frac{H^\circ - H}{RT^2}, \quad (252)$$

or

$$\left(\frac{\partial \log f'}{\partial T}\right)_P = \frac{H^\circ - H}{RT^2}. \quad (253)$$

A physical significance can be attached to the quantity  $H^\circ - H$  occurring in (251), (252) and (253) in terms of the Joule-Thomson

effect. Suppose the gas at the given pressure  $P$  be forced through a plug, the pressure at the other side being so low that the gas is perfect. Then  $H^\circ - H$  is the quantity of heat that must be supplied to each mole of gas forced through the plug, in order that its temperature may remain unchanged.

*Slightly Imperfect Single Gas.*—For all except very high pressures the deviations of most gases from perfection are small and it is often sufficient to retain only the terms of lowest order in  $P$  of those expressing deviations from perfection. In this case the formulæ simplify considerably. The equation of state (237) becomes

$$PV = RT\{1 + B \cdot P\}. \quad (254)$$

For the chemical potential (254) leads to

$$\mu = \mu^\circ(T) + RT\{\log P + B \cdot P\}, \quad (255)$$

and for the compressibility (254) leads to

$$\kappa = \frac{1}{P}\{1 - B \cdot P\}. \quad (256)$$

The formula for the fugacity (245) becomes

$$\log P^* = \log P + B \cdot P. \quad (257)$$

For the two kinds of activity coefficients  $f'$  and  $f$  the formulæ (246) and (247) become

$$\log f' = B \cdot P, \quad (258)$$

$$\log f = 2B \cdot P. \quad (259)$$

*Condensed Phases.*—For condensed phases (solids and liquids) as opposed to gases the compressibility may to a first approximation be regarded as zero and to a second approximation as independent of the pressure at a given temperature. At all ordinarily occurring pressures this approximation is amply sufficient, and we shall therefore use it. For the molar volume we have, at given temperature by integration of (180.1),

$$V = V^*e - \kappa P, \quad (260.1)$$

where  $\kappa$  the compressibility and  $V^*$  the molar volume at zero pressure depend only on the temperature and the nature of the system. Or with sufficient accuracy, since  $\kappa P$  will always be so small that its square may be neglected,

$$V = V^*\{1 - \kappa P\}. \quad (260.2)$$

For the volume of a condensed phase of a single species containing  $n$  moles we have

$$V = nV^*\{1 - \kappa P\}, \quad (261)$$

and for given  $n$

$$dV = -nV^*\kappa dP. \quad (262)$$

For a given temperature the Helmholtz free energy  $F$  is according to (27.2) given by

$$F = - \int^P PdV. \quad (263)$$

Substituting from (262) into (263) we obtain

$$\begin{aligned} F &= \int^P nV^*\kappa PdP \\ &= n\{\mu^*(T) + \tfrac{1}{2} V^*\kappa P^2\}, \end{aligned} \quad (264)$$

where  $\mu^*(T)$  depends on the temperature, but not on the pressure.

The Gibbs free energy  $G$  is given by

$$\begin{aligned} G &= F + PV \\ &= n\{\mu^*(T) + PV^*(1 - \tfrac{1}{2}\kappa P)\}, \end{aligned} \quad (265)$$

using (264) and (261).

For the chemical potential we have by (29.3) and (265)

$$\begin{aligned} \mu &= \left(\frac{\partial G}{\partial n}\right)_{T,P} \\ &= \mu^*(T) + PV^*(1 - \tfrac{1}{2}\kappa P). \end{aligned} \quad (266.1)$$

Differentiating (266.1) with respect to  $P$ , and using (260.2), we find

$$\left(\frac{\partial \mu}{\partial P}\right)_T = V^*\{1 - \kappa P\} = V, \quad (266.2)$$

in agreement with the general formula (153).

*Relation between Chemical Potential and Vapour Pressure of Condensed Phases at same Temperature.*—The fundamental property of the chemical potential of a given species is that it has the same value in two phases in equilibrium as regards this species. In particular the chemical potential of any pure solid or liquid is the same as that of the vapour in equilibrium with it. Hence, as long as the vapour behaves as a perfect gas it follows from (216) that the chemical potential of any pure solid or liquid is given by

$$\mu = \mu^\circ(T) + RT \log p, \quad (267)$$

where  $p$  denotes the "saturated vapour pressure" of the solid or liquid, that is the pressure of vapour in equilibrium with the solid or liquid, and  $-\mu^\circ(T)$  depends on the temperature only, having the same value for all phases, solid or liquid, of the same pure substance.

More generally, even if the vapour is not a perfect gas, we may write for the chemical potential of any phase of one component

$$\mu = \mu^\circ(T) + RT \log p^*, \quad (268)$$

where  $p^*$  is the "saturated vapour fugacity" that is the fugacity of the vapour in equilibrium with the given phase.  $\mu^\circ(T)$  depends on the temperature only, having the same value for all phases, whether solid or liquid, of the given pure substance.

*One Component in Two Phases.*—According to the phase rule (106), a system of one component existing in two phases in complete equilibrium has one degree of freedom. That is to say, that temperature and pressure are variable, but not independently. If equilibrium is to be maintained, there must be a relation between the variations of temperature and pressure. This relation is obtainable directly from equation (150)

$$\left(\frac{\partial P}{\partial T}\right)_v = \left(\frac{\partial S}{\partial V}\right)_T, \quad (269)$$

by applying it to a system consisting of two phases of one component in equilibrium. Firstly, we may notice that for such a system the pressure is determined entirely by the temperature and is independent of the volume, which merely depends on the quantities of the two phases. We may therefore replace  $\left(\frac{\partial P}{\partial T}\right)_v$

by  $\frac{dP}{dT}$ . Secondly, in such a system at a definite temperature, the only change possible consistent with equilibrium is an increase of one phase at the expense of another, the nature of the two phases remaining unchanged. We may therefore replace  $\left(\frac{\partial S}{\partial V}\right)_T$

by  $\frac{\Delta S}{\Delta V}$ , where the operator  $\Delta$  denotes excess of the value in the second phase over the value in the first. Thirdly, since the two phases are in equilibrium, we have, according to (82),

$$\Delta\mu = 0, \quad (270)$$

and so

$$\Delta S = \frac{\Delta H - \Delta\mu}{T} = \frac{\Delta H}{T} = \frac{L}{T}, \quad (271)$$

where  $L$  is the molar heat of transformation at equilibrium. Taking all these considerations into account, we have the condition

$$\frac{dP}{dT} = \frac{L}{T\Delta V}. \quad (272)$$

For equilibrium between a solid and a liquid we have, for the dependence of the freezing-point  $T$  on the pressure  $P$

$$\frac{dT}{dP} = \frac{(V^L - V^S)T}{L_F}, \quad (273)$$

where  $V^L$ ,  $V^S$  are the molar volumes of the liquid and solid respectively and  $L_F$  is the molar heat of fusion. The expression on the right may have either sign and is small. Except for high pressures, the temperature of fusion or the "freezing-point" may be considered independent of the pressure.

For equilibrium between a pure liquid and its vapour we have

$$\frac{dP}{dT} = \frac{L_E}{T(V^G - V^L)}, \quad (274)$$

where  $V^G$ ,  $V^L$  are the molar volumes of the vapour and the liquid respectively and  $L_E$  the molar heat of evaporation (at equilibrium and so at constant pressure). Provided the vapour is a perfect gas we may substitute from (199) for  $V^G$  and obtain for the dependence of the vapour pressure  $p$  on the temperature

$$\frac{dp}{dT} = \frac{L_E}{T\left(\frac{RT}{p} - V^L\right)}. \quad (275)$$

But  $V^L$  for a liquid is usually extremely small compared with  $V^G$  for a vapour, and so may be neglected; (275) then simplifies to

$$\frac{dp}{dT} = \frac{L_E p}{RT^2}, \quad (276)$$

or

$$\frac{d \log p}{dT} = \frac{L_E}{RT^2}. \quad (277)$$

This is known as the Clapeyron-Clausius formula. An exactly analogous formula holds for the vapour pressure of a solid,  $L_E$  then denoting the heat of sublimation.

*Molar Heat Capacities of Two Phases in Equilibrium.*—Suppose we have two phases of a single component in equilibrium and we heat both through a temperature interval  $dT$ , neither at

constant volume nor at constant pressure, but altering the pressure so that it is at each temperature the equilibrium pressure for the two phases at that temperature. The quantity of heat absorbed per mole in each phase will evidently be proportional to the number of moles and to  $dT$ . For this quantity we may therefore write in the case of one of the two phases

$$q = nC_{Eq}dT, \quad (278)$$

where  $n$  is the number of moles in the one phase and  $C_{Eq}$  is the "molar heat capacity at two phase equilibrium" in the one phase.

As the change is reversible, we may write, instead of (278),

$$TdS = nC_{Eq}dT. \quad (279)$$

But for the change in question

$$dS = \left\{ \left( \frac{\partial S}{\partial T} \right)_P + \left( \frac{\partial S}{\partial P} \right)_T \frac{dP}{dT} \right\} dT. \quad (280)$$

Comparing (279) and (280), we see that

$$C_{Eq} = \frac{T}{n} \left\{ \left( \frac{\partial S}{\partial T} \right)_P + \left( \frac{\partial S}{\partial P} \right)_T \frac{dP}{dT} \right\}. \quad (281)$$

Substituting from (142), (151), and (272) into (281), we obtain finally

$$C_{Eq} = C_P - \left( \frac{\partial V}{\partial T} \right)_P \frac{L}{\Delta V}, \quad (282)$$

where  $L$  denotes the molar heat of change of phase and  $P$  is the equilibrium pressure between the two phases.

The most important case is that of equilibrium between a liquid and its vapour. The quantities  $C_{Eq}$  are then called the "molar heat capacities at saturation" denoted by  $C_{\text{sat}}$ . Assuming that the vapour behaves as a perfect gas, and neglecting the molar volume of the liquid phase compared with that of the vapour phase, (282) takes the form

$$\begin{aligned} C_{\text{sat}} &= C_P - \left( \frac{\partial V}{\partial T} \right)_P \frac{L_E}{V_g} \\ &= C_P - \left( \frac{\partial V}{\partial T} \right)_P \frac{L_E P}{RT}, \end{aligned} \quad (283)$$

where  $L_E$  is the molar heat of evaporation. This formula can be applied to either the vapour or the liquid, but the importance of the second term on the right is very different in the two cases.

For the vapour, assuming it to be a perfect gas, we have by (199)

$$\left(\frac{\partial V}{\partial T}\right)_P = \frac{V}{T} = \frac{R}{P}, \quad (284)$$

and so substituting in (283)

$$C_{\text{sat}}^G = C_P^G - \frac{L_E}{T}, \quad (285)$$

where the symbol  $G$  in the index position denotes the vapour phase. The second term on the right may be numerically greater than the first, as indeed it is for water. In this case,  $C_{\text{sat}}^G$  is negative. This means that to raise the temperature of saturated steam, varying its pressure so as to keep it saturated, heat has to be withdrawn and not supplied.

For the liquid phase, on the other hand, the second term on the right of (283) is generally very small, and with sufficient accuracy we may omit it and write

$$C_{\text{sat}}^L = C_P^L, \quad (286)$$

where the symbol  $L$  in the index position refers to the liquid phase.

*Temperature Coefficients of Heats of Evaporation and of Fusion.*—To obtain the temperature coefficient of a heat of evaporation at equilibrium we may not apply either of Kirchhoff's formulæ (177) or (179) directly because the process of reversible evaporation at two different temperatures takes place neither between the same volume limits nor at the same pressure. (Such an unwarranted application of Kirchhoff's formula occurs in numerous text-books.) We proceed as follows. For the process of evaporation of one mole the heat absorbed is  $L_E$  and, since the process is reversible,

$$L_E = T\Delta S, \quad (287)$$

and so

$$\begin{aligned} T \frac{d}{dT} \left( \frac{L_E}{T} \right) &= T \frac{\partial}{\partial T} \Delta S \\ &= T \Delta \frac{\partial S}{\partial T} \\ &= \Delta C_{\text{sat}}. \end{aligned} \quad (288)$$

Using the values given by (285) and (286) for  $C_{\text{sat}}^G$  in the vapour phase and  $C_{\text{sat}}^L$  in the liquid phase, we obtain

$$T \frac{d}{dT} \left( \frac{L_E}{T} \right) = C_P^G - \frac{L_E}{T} - C_P^L, \quad (289)$$



whence

$$\frac{dL_E}{dT} = C_P^G - C_P^L, \quad (290)$$

a relation formally similar to that of Kirchhoff. But Kirchhoff's formula (179) holds for a process occurring at a fixed pressure independent of the temperature. The process of evaporation at equilibrium is not of this type. Moreover, (290) is not exact, but is obtained only by ignoring the second term in the formula (283) for  $C_{\text{sat}}^L$  in the liquid phase. The justification for ignoring this term is that for liquids it happens to be small compared with the first.

To obtain the temperature coefficient of the heat of fusion (at equilibrium between the solid and liquid phases) we proceed similarly and obtain in analogy with (288)

$$T \frac{d}{dT} \left( \frac{L_F}{T} \right) = \Delta C_{Eq}, \quad (291)$$

where  $L_F$  is the molar latent heat of fusion. The values of  $C_{Eq}$  for the two phases are, according to (282), given by

$$C_{Eq} = C_P - \left( \frac{\partial V}{\partial T} \right)_P \frac{L_F}{\Delta V}. \quad (292)$$

Substituting (292) into (291), we obtain

$$T \frac{d}{dT} \left( \frac{L_F}{T} \right) = \Delta C_P - \frac{L_F}{\Delta V} \left( \frac{\partial \Delta V}{\partial T} \right)_P, \quad (293)$$

or

$$\frac{dL_F}{dT} = \Delta C_P + \frac{L_F}{T} - \frac{L_F}{T} \left( \frac{\partial \log \Delta V}{\partial \log T} \right)_P. \quad (294)$$

This formula is due to Planck. The last term on the right will generally be very small compared with the second, and may then be neglected. We then have

$$\frac{dL_F}{dT} = \Delta C_P + \frac{L_F}{T}. \quad (295)$$

Of the two terms on the right, either may be the numerically greater. We thus have an equation which is not even approximately of the form of Kirchhoff's formulæ.

It need hardly be mentioned that formula (295) may be equally applied to the equilibrium between two solid phases,  $L_F$  then denoting the heat of transformation.

*One Component in Three Phases.*—For a system of one component in three phases in equilibrium the phase rule (107)

predicts zero degrees of freedom. Suppose the vapour pressure of the liquid is given by the relation

$$p = p_1(T), \quad (296)$$

and that of the solid by

$$p = p_2(T). \quad (297)$$

For such values of  $T$  as  $p_1 > p_2$  the liquid will have the greater vapour pressure, and so will be unstable relative to the solid. For such values of  $T$  as  $p_2 > p_1$ , the reverse is the case. For the value of  $T$  that  $p_1 = p_2$ , the three phases solid, liquid and vapour will all be in mutual equilibrium, the equilibrium pres-

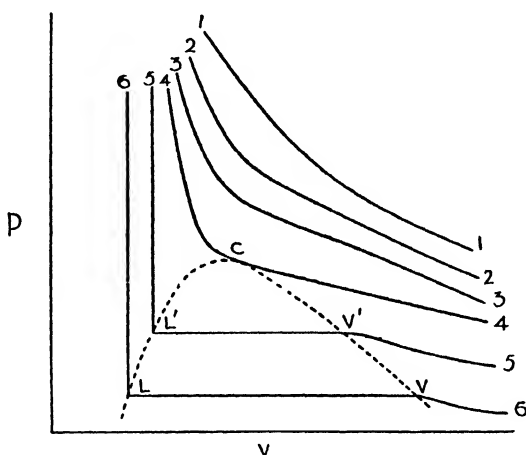


FIG. 3.

sure being given equally by (296) and (297). Such an equilibrium condition is called a "triple point". Triple points may also exist for a single component existing as two solid phases and one liquid phase, or two solid phases and one vapour phase, or three solid phases. More rarely we may have two liquid phases and a vapour phase.

*Critical Point.*—If we plot the pressure against the volume for one mole of a single substance at constant temperature, we obtain at the highest temperatures a rectangular hyperbola with the co-ordinate axes as asymptotes, for at these temperatures the substance behaves as a perfect gas. This is illustrated by curve 1 in Fig. 3. At somewhat less high temperatures the isothermal curves show departures from rectangular hyperbolæ at

the end corresponding to high pressures. As the temperature decreases these departures from ideality become more pronounced. This is illustrated by curves 2 and 3. At low temperatures, on the other hand, the curve consists of three smooth parts with sharp breaks between them. This is illustrated by curves 5 and 6. The low pressure parts of these curves still approximate more or less to rectangular hyperbolæ, these representing the substance in the vapour state. The high pressure parts of these curves, on the other hand, represent the liquid state, and are almost vertical, corresponding to the comparatively small compressibility in the liquid state. These two parts of each curve are joined by a straight horizontal part representing liquid and vapour phase in equilibrium, the height above the volume axis representing the saturated vapour pressure at the given temperature. Curve 4 represents the transition between the gas curves, such as 2 and 3 on the one hand, and the liquid-vapour curves of type 5 and 6 on the other. The straight horizontal part of the latter curves is in curve 4 reduced to the horizontal point of inflexion  $C$ . The dotted curve  $LL'C$  is the locus of the points representing the liquid phase under the pressure of its vapour, and the dotted curve  $VV'C$  is the locus of the points representing the saturated vapour. As the temperature increases the molar volume of the liquid at the pressure of its vapour increases, while the molar volume of the saturated vapour decreases. When the temperature corresponding to curve 4 is reached the molar volumes of liquid and of vapour are both represented by the same point  $C$ . The liquid and vapour states are then no longer distinguishable. The state represented by  $C$  is called the "critical state". The temperature of curve 4 is the "critical temperature," the pressure and molar volume represented by  $C$  are the "critical pressure" and "critical volume".

Above the critical temperature the substance can exist in only one state, the gaseous. Below the critical temperature it can exist in two states, the liquid with a molar volume less than the critical volume, and the vapour with a molar volume greater than the critical. The critical pressure is the highest pressure at which the two phases, liquid and vapour, can co-exist in equilibrium.

*Continuity of State.*—In Fig. 4 the pressure is plotted against the volume for one mole of a single component at a temperature below the critical temperature. The portion  $KL$  represents the liquid state, the portion  $VW$  the vapour state, and the horizontal portion  $LV$  the two phase system liquid vapour.

At the given temperature the substance can only be brought from the liquid state to the vapour state, or, conversely, by a

change during part of which two separate phases will be present. By introducing temperature alterations, however, it is possible to bring the substance from the vapour state represented by  $W$  to the liquid state represented by  $K$  by a continuous change throughout which there is never more than one phase present. It is only necessary to raise the temperature above the critical temperature, keeping the volume sufficiently greater than the critical volume, then compress the fluid to a volume below the critical volume, keeping the temperature above the critical temperature, and finally cool the liquid to its original temperature, keeping the volume sufficiently below the critical volume. This possibility of continuity between the liquid and vapour states was first realised by James Thomson, and he suggested

that the portions  $KL$  and  $VW$  of the isotherm were actually parts of one smooth curve, such as  $KLMONVW$ . In point of fact, states corresponding to the portion  $VN$  are realisable as "super-saturated" vapour, and under certain circumstances the same may be true of the portion  $LM$  representing "super-heated" liquid. Each of these portions represents states stable with respect to infinitesimal variations, but unstable relative to the two phase

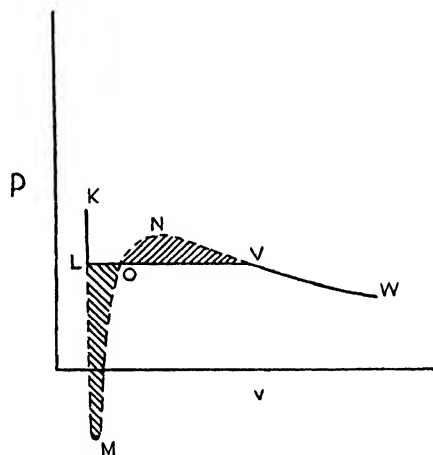


FIG. 4.

system liquid + saturated vapour. The portion of the curve  $MON$ , on the other hand, represents states absolutely unstable, since here

$$\frac{\partial V}{\partial P} > 0, \quad (298)$$

and, according to (79), such states are never realisable.

Although the states represented by points on the curve  $LMONV$  are unstable, either relatively or absolutely, still they are equilibrium states. It follows that the sequence of states represented by the curve  $LMONV$  corresponds to a reversible process. The change in the chemical potential  $\mu$  of the fluid in

passing through this sequence of states is, according to (153), given by

$$\begin{aligned}\mu^V - \mu^L &= \int \left( \frac{\partial \mu}{\partial P} \right)_T dP \\ &= \int V dP,\end{aligned}\quad (299)$$

where the integrals are to be evaluated along the curve  $LMONV$ . But since the two states represented by  $L$  and  $V$  can exist in equilibrium with each other, we have, according to (82),

$$\mu^V = \mu^L. \quad (300)$$

From (299) and (300) we deduce

$$\int V dP = 0, \quad (301)$$

where the integral is to be evaluated along the curve  $LMONV$ . The geometrical significance of (301) is that the two hatched surfaces  $LMO$  and  $ONV$  are of equal area.

*Two Phases at Different Pressures.*—In our previous considerations of the equilibrium between two phases of one component, we have assumed that the equilibrium was complete so that the phases were at the same pressure. The chemical equilibrium between two phases of one component at different pressures is also of theoretical interest. Let us denote the two phases in equilibrium by the indices  $\alpha$  and  $\beta$ . Then the equilibrium condition determining the change of one phase to the other is, according to (82),

$$\mu^\alpha = \mu^\beta. \quad (302)$$

If we alter the common temperature  $T$  of the two phases and the pressures  $P^\alpha$  and  $P^\beta$  of the two phases, the condition for maintenance of equilibrium is

$$d\mu^\alpha = d\mu^\beta, \quad (303)$$

or

$$\left( \frac{\partial \mu}{\partial T} \right)_P^\alpha dT + \left( \frac{\partial \mu}{\partial P} \right)_T^\alpha dP^\alpha = \left( \frac{\partial \mu}{\partial T} \right)_P^\beta dT + \left( \frac{\partial \mu}{\partial P} \right)_T^\beta dP^\beta. \quad (304)$$

Substituting from (152) and (153) into (304) we obtain

$$-S^\alpha dT + V^\alpha dP^\alpha = -S^\beta dT + V^\beta dP^\beta. \quad (305)$$

But we have from (25), (29.3) and (302)

$$\begin{aligned} T(S^\beta - S^\alpha) &= (H^\beta - H^\alpha) - (\mu^\beta - \mu^\alpha) \\ &= H^\beta - H^\alpha \\ &= L, \end{aligned} \quad (306)$$

where  $L$  is the molar heat of change from phase  $\alpha$  to phase  $\beta$ . We may therefore write (305) in the form

$$\frac{LdT}{T} + v^\alpha dP^\alpha = v^\beta dP^\beta. \quad (307)$$

As we are allowing the two phases to be at different pressures, the phase rule gives two degrees of freedom. Thus only two of the three quantities  $T$ ,  $P^\alpha$ ,  $P^\beta$  are independent. We shall now consider two special cases of (307).

First suppose the temperature fixed. We then have

$$dT = 0 \quad v^\alpha dP^\alpha = v^\beta dP^\beta. \quad (308)$$

The changes of pressure on the two phases required to maintain equilibrium are inversely proportional to the molar volumes in the respective phases. The most important example of this is the dependence of the saturated vapour pressure  $p$  of a liquid (or solid) on the hydrostatic pressure  $P$  on the liquid (or solid). In this case we have

$$\frac{dp}{dP} = \frac{v^L}{v^G} \quad (309)$$

where the index  $L$  refers to the liquid, and the index  $G$  refers to the vapour. If the vapour is a perfect gas, we can substitute from (199) into (309) and obtain

$$\frac{dp}{dP} = \frac{p}{RT} v^L, \quad (310)$$

or

$$RT \frac{d \log p}{dP} = v^L. \quad (311)$$

Formula (311) could be obtained more directly by making use of the fact that, according to (267), the chemical potential  $\mu^L$  of the liquid phase is related to the vapour pressure by

$$\mu^L = \mu^\circ(T) + RT \log p. \quad (312)$$

Substituting from this in the formula (153) for the pressure derivative of the chemical potential

$$\left(\frac{\partial \mu^L}{\partial P}\right)_T = v^L, \quad (313)$$

we obtain directly

$$RT \left(\frac{\partial \log p}{\partial P}\right)_T = v^L, \quad (314)$$

the same as (311).

As the second special case of (307), let us suppose the pressure  $P^\alpha$  of the phase  $\alpha$  kept constant, while the common temperature  $T$  of the two phases and the pressure  $P^\beta$  of the phase  $\beta$  are varied. Formula (307) now becomes

$$dP^\alpha = 0 \quad \frac{LdT}{T} = v^\beta dP^\beta, \quad (315)$$

a formula due to G. N. Lewis. The most important example of this is the dependence of the saturated vapour pressure  $p$  of a liquid on the temperature when the pressure  $P$  on the liquid is kept constant. We then have

$$\frac{dp}{dT} = \frac{L_E}{TV^g}. \quad (316)$$

$L_E$  is the molar heat of evaporation, and  $V^g$  is the molar volume of the vapour. If the vapour is a perfect gas, then, according to (199), formula (316) takes the form

$$\frac{d \log p}{dT} = \frac{L_E}{RT^2}. \quad (317)$$

It is to be observed that the exact formula (317), for the temperature coefficient of the vapour pressure of a liquid kept at constant hydrostatic pressure, is identical with formula (277) obtained for the case that the hydrostatic pressure of the liquid was the same as that of the vapour, but the latter formula was not quite exact, as it involved neglecting the molar volume of the liquid compared with the molar volume of the vapour. The exact formula was (275). That the difference between the exact formulæ (275) and (317) is negligible is due to the fact that to affect the vapour pressure appreciably by change of the hydrostatic pressure at constant temperature, one requires hydrostatic pressures considerably greater than the vapour pressure itself.

## NOTES AND REFERENCES

*Perfect Gases.*—The derivation of the laws of perfect gases from molecular kinetic considerations is given in any text-book of statistical mechanics, e.g. Jeans' "Dynamical Theory of Gases" and Fowler's "Statistical Mechanics".

*Imperfect Gases.*—The only discussion of the form of the equation of state of imperfect gases that is entirely sound is that in Fowler's "Statistical Mechanics".

*Fugacity and Activity Coefficient.*—These functions were invented by G. N. Lewis. The original papers are *Proc. Am. Acad.*, **37**, 49 (1901), and *Z. Physikal. Chem.*, **38**, 205 (1901).

*Dependence of Heats of Evaporation and of Fusion on Temperature.*—Of fifteen text-books and reference books consulted, only three give a correct derivation of formula (294). These are Planck's "Thermodynamics," Muller-Pouillet, Vol. III, and Schottky, Ulich and Wagner's "Thermodynamik".

*Dependence of Vapour Pressure on Temperature* at constant external pressure on the liquid. The original derivation of formulæ (316) and (317) are given by Lewis in *Proc. Am. Acad.*, **37**, 49 (1901), and *Z. Physikal. Chem.*, **38**, 205 (1901).



## CHAPTER IV

### GASEOUS MIXTURES

*Partial Vapour Pressures.*—In the treatment of gaseous mixtures it is convenient to define quantities known as the “partial vapour pressures” of the various species. Since the pressure is not a capacity factor, but an intensity factor, the “partial vapour pressures” are not “partial molar” quantities. We define the partial vapour pressure  $p_i$  of the species  $i$  by

$$p_i = N_i P. \quad (318)$$

Owing to the identity (99) the partial vapour pressures satisfy identically the relation

$$\sum_i p_i = P. \quad (319)$$

In the particular case of a single gas the partial vapour pressure  $p_i$  is the same as the total pressure  $P$ .

*Perfect Gaseous Mixtures.*—A gaseous mixture may be defined as perfect if the chemical potential  $\mu_i$  of each species is the same function of the temperature  $T$  and the partial vapour pressure  $p_i$  of the species  $i$  as it is for the single perfect gas. According to (215) and (318) this condition may be written

$$\begin{aligned} \mu_i &= \int^T C_i^\circ dT - T \int^T C_i^\circ d \log T + RT \log p_i \\ &= \int^T C_i^\circ dT - T \int^T C_i^\circ d \log T + RT \log P + RT \log N_i, \end{aligned} \quad (320)$$

where  $C_i^\circ$  denotes the molar heat capacity at constant pressure of the species  $i$  as a single perfect gas. All the properties common to perfect gaseous mixtures are deducible from (320). According to (320) an alternative way of writing the formula for  $\mu_i$  is

$$\begin{aligned} \mu_i &= \mu_i^\circ(T) + RT \log p_i \\ &= \mu_i^\circ(T) + RT \log P + RT \log N_i, \end{aligned} \quad (321)$$

where  $\mu_i^\circ(T)$  depends only on the temperature and according to (173)

$$\frac{d\mu_i^\circ/T}{dT} = - \frac{H_i^\circ}{T^2}, \quad (322)$$

where  $H_i^\circ$  is the value of  $H_i$  for the single gas  $i$  at the given temperature.

*Dalton's Law of Partial Pressures and the Law of Membrane Equilibrium.*—By differentiation of (320) with respect to  $P$  we obtain, according to (153), for the partial molar volume  $V_i$  of the species  $i$

$$V_i = \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_i, n_j} = \frac{RT}{P}. \quad (323)$$

Hence by (119) we have for the total volume

$$V = \sum_i n_i V_i = \sum_i n_i \frac{RT}{P}, \quad (324)$$

or

$$P = \sum_i \frac{n_i}{V} RT. \quad (325)$$

From (325) and the definition (318) of the partial pressure  $p_i$  we obtain

$$p_i = \frac{n_i}{V} RT. \quad (326)$$

These last two relations express one of the most important properties of perfect gaseous mixtures, the property generally known as Dalton's Law of partial pressures. Important as is this property it cannot by itself replace (320) as the definition of a perfect gaseous mixture. It would have to be supplemented by the following law: if two perfect gaseous mixtures be separated by a membrane permeable to some of the species and impermeable to others, then the condition for equilibrium across the membrane of the species  $i$  to which the membrane is supposed permeable is equality of the partial vapour pressures  $p_i$  of  $i$  on the two sides of the membrane. While this law is independent of Dalton's law of partial pressures, both laws are directly derivable from (320), which we have therefore chosen as the definition of a perfect gaseous mixture. The derivation of Dalton's law we have already given; that of the membrane equilibrium is derived at once by substituting the value of  $\mu_i$  given by (321) in the general condition (90) of membrane equilibrium

$$\mu_i^\alpha = \mu_i^\beta. \quad (327)$$

We obtain directly

$$p_i^\alpha = p_i^\beta. \quad (328)$$

*Heat Content and Heat Capacities.*—By differentiation with respect to  $T$  of (321) we obtain for the partial molar heat content  $H_i$ , according to (173),

$$\begin{aligned} H_i &= -T^2 \left( \frac{\partial \mu_i / T}{\partial T} \right)_{P, n_i, n_j} \\ &= -T^2 \left( \frac{d\mu_i^\circ / T}{dT} \right)_{P, n_i, n_j} \\ &= \int^T C_i^\circ dT. \end{aligned} \quad (329)$$

But according to the general relation (146) we have

$$H_i = \int^T C_i dT, \quad (330)$$

where  $C_i$  is the partial molar heat content at constant pressure in the mixture. Since (329) and (330) hold simultaneously for all temperatures it follows that

$$C_i = C_i^\circ \quad (331)$$

$$H_i = H_i^\circ \quad (332)$$

where the symbol  $^\circ$  in the index position refers to the value for the pure perfect gas. That is to say that the partial molar heat content  $H_i$  and the partial molar heat capacity  $C_i$  are independent of the composition. They are also independent of the pressure from our definition of a single perfect gas since we know that this holds for  $H_i^\circ$  and  $C_i^\circ$ . Thus for a given species  $i$ ,  $H_i$  and  $C_i$  depend only on the temperature.

From the relations (21), (332) and (323) it follows that

$$E_i = E_i^\circ, \quad (333)$$

and differentiation of this with respect to  $T$  gives

$$C_{V_i} = C_{V_i}^\circ. \quad (334)$$

Thus the partial molar energies  $E_i$  and partial molar heat capacities at constant volume  $C_{V_i}$  are also independent of the composition as well as of the pressure or volume. They therefore depend only on the temperature.

It follows that for perfect gaseous mixtures as for single perfect gases

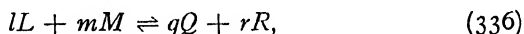
$$C_{P_i} - C_{V_i} = R. \quad (335)$$

An important physical consequence of (332) and (333) is that perfect gases mix at constant temperature without any

evolution or absorption of heat. It does not matter whether the gases are initially at the same or different pressures provided they are at the same temperature.

*Entropy.*—To prove that the partial molar heat content  $H_i$  has the same value in a mixture as for the single gas at the same temperature and same partial pressure, we differentiated (320) with respect to  $T$  and used (173). If instead of (173) we use (152) in a similar manner, we obtain the result that the partial molar entropy  $S_i$  has the same value in a mixture as in the single gas at the same temperature and the same partial vapour pressure.

*Law of Mass Action.*—We will consider the homogeneous chemical equilibrium of the reaction



where  $L, M, Q, R$  represent moles of the reacting species and  $l, m, q, r$  are small integers. The extension of the formulæ to more or less complicated reactions will be obvious. According to (97) the general form of the condition for homogeneous equilibrium is

$$l\mu_L + m\mu_M = q\mu_Q + r\mu_R. \quad (337)$$

If the reacting species are all perfect gases, we may substitute into (337) the values given by (321) for the chemical potentials. We thus obtain

$$\begin{aligned} lRT \log p_L + l\mu_L^\circ + mRT \log p_M + m\mu_M^\circ \\ = qRT \log p_Q + q\mu_Q^\circ + rRT \log p_R + r\mu_R^\circ, \end{aligned} \quad (338)$$

or

$$RT \log \frac{(p_Q)^q \cdot (p_R)^r}{(p_L)^l \cdot (p_M)^m} = l\mu_L^\circ + m\mu_M^\circ - q\mu_Q^\circ - r\mu_R^\circ, \quad (339)$$

where  $\mu_L^\circ, \mu_M^\circ, \mu_Q^\circ, \mu_R^\circ$  are functions of the temperature only. We may therefore write instead of (339)

$$RT \log \frac{(p_Q)^q \cdot (p_R)^r}{(p_L)^l \cdot (p_M)^m} = RT \log K(T), \quad (340)$$

or

$$\frac{(p_Q)^q \cdot (p_R)^r}{(p_L)^l \cdot (p_M)^m} = K(T), \quad (341)$$

where  $K(T)$  called the "equilibrium constant" of the reaction depends only on the temperature. Formula (341) is the law of mass action for perfect gases.

Since the value of  $K$  is clearly not arbitrary, it appears that,

when there is a possibility of a chemical reaction involving the species  $L, M, Q, R$ , the choice of standard state of zero for the chemical potential is not independent for these species. The above deduction is on this account possibly open to criticism. We will therefore deduce the law of mass action (341) by a somewhat modified argument not involving standard states.

Consider two sets of definite values of the partial vapour pressures  $p_i$  denoted respectively by a single dash  $p_i'$  and by a double dash  $p_i''$ . Then for each species  $i$  we have, independently of any choice of the state of zero,

$$\mu_i'' - \mu_i' = RT \log \frac{p_i''}{p_i'}. \quad (342)$$

Now suppose that the set of values  $p_i'$  and likewise the set of values  $p_i''$  each corresponds to a state of chemical equilibrium at the same temperature  $T$ . Then according to (97)

$$l\mu_L' + m\mu_M' = q\mu_Q' + r\mu_R', \quad (343.1)$$

$$l\mu_L'' + m\mu_M'' = q\mu_Q'' + r\mu_R''. \quad (343.2)$$

By subtraction and substitution of (342) we obtain

$$\begin{aligned} lRT \log \frac{p_L''}{p_L'} + mRT \log \frac{p_M''}{p_M'} \\ = qRT \log \frac{p_Q''}{p_Q'} + rRT \log \frac{p_R''}{p_R'}, \end{aligned} \quad (344)$$

or

$$\frac{(p_Q')^q \cdot (p_R')^r}{(p_L')^l \cdot (p_M')^m} = \frac{(p_Q'')^q \cdot (p_R'')^r}{(p_L'')^l \cdot (p_M'')^m}. \quad (345)$$

As a similar relation must hold for any other sets of equilibrium  $p_i$  values at the same temperature, it follows that (345) is equivalent to (341).

The law of mass action for perfect gases (341) can be put into other slightly different forms. According to the definition (318) of the partial pressures, instead of (341) we may write

$$\begin{aligned} \frac{(N_Q)^q \cdot (N_R)^r}{(N_L)^l \cdot (N_M)^m} &= K \cdot P^{l+m-q-r} \\ &= K'(T, P), \end{aligned} \quad (346)$$

where  $K'$  is not a function of  $T$  only but is proportional to  $P^{l+m-q-r}$ . Thus  $K'$  increases or decreases with increase of the total pressure according as there is a decrease or increase in

the number of molecules as the reaction (336) proceeds from left to right.

Again, substituting in (341) the equation of state (326) of perfect gases, we obtain

$$\frac{\left(\frac{n_Q}{V}\right)^q \cdot \left(\frac{n_R}{V}\right)^r}{\left(\frac{n_L}{V}\right)^l \cdot \left(\frac{n_M}{V}\right)^m} = (RT)^{l+m-q-r} K$$

$$= K''(T), \quad (347)$$

where  $K''$  depends on the temperature only.

$K(T)$ ,  $K'(T, P)$  and  $K''(T)$  are all three commonly called "equilibrium constants".

*Temperature Coefficients of Equilibrium Constants.*—By comparing (340) with (339), and using (322), we obtain for the temperature coefficient of  $K$

$$\frac{d \log K}{dT} = \frac{qH_Q + rH_R - lH_L - mH_M}{RT^2}$$

$$= \frac{L_P}{RT^2}, \quad (348)$$

where  $L_P$  is the heat of reaction at constant pressure of the forward reaction of (336). We recall that we have chosen to define the heat of reaction  $L_P$  as the heat absorbed when the reaction takes place; this convention, though not universal, has the advantage of being the same as regards sign as that according to which the expressions "heat of fusion" and "heat of evaporation" are defined. Since the value of the partial molar heat content  $H_i$  of a perfect gas depends only on the temperature and not on the pressure, the heat of reaction  $L_P$  is also independent of the pressure.

From (346) it is obvious that

$$\left(\frac{\partial \log K'}{\partial T}\right)_P = \frac{d \log K}{dT}, \quad (349)$$

and so according to (348)

$$\left(\frac{\partial \log K'}{\partial T}\right)_P = \frac{L_P}{RT^2}. \quad (350)$$

For the temperature coefficient of  $K''$  we have from (347) and (348)

$$\begin{aligned}
 \frac{d \log K''}{dT} &= \frac{d \log K}{dT} + \frac{l + m - q - r}{T} \\
 &= \frac{L_P - (q + r - l - m)RT}{RT^2} \\
 &= \frac{L_V}{RT^2},
 \end{aligned} \tag{351}$$

where  $L_V$  is the heat of reaction at constant volume. For according to the definitions (174) and (175) of  $L_V$  and  $L_P$  we have

$$\begin{aligned}
 L_P - L_V &= \Delta H - \Delta E \\
 &= \Delta(PV) \\
 &= (q + r - l - m)RT,
 \end{aligned} \tag{352}$$

using the equation of state of a perfect gas (324).

*Imperfect Gaseous Mixtures.*—If in a mixture of gases the species present do not all obey the law (321), the mixture is not perfect. In this case we may extend to such a mixture the conceptions of “fugacity” and “activity coefficient” already defined for a single imperfect gas. The fugacity  $p_i^*$  of the species  $i$  in the mixture is defined by

$$\mu_i = \mu_i^\circ(T) + RT \log p_i^*, \tag{353}$$

where  $\mu_i^\circ(T)$  is a function of the temperature only, together with one of the conditions

$$\frac{p_i^*}{p_i} \rightarrow 1 \quad \text{as } P \rightarrow 0, \tag{354.1}$$

or

$$\frac{p_i^* V}{n_i R T} \rightarrow 1 \quad \text{as } P \rightarrow 0, \tag{354.2}$$

these two being equivalent, since at infinitely small pressures all gaseous mixtures become perfect.

The two kinds of activity coefficient  $f_i'$  and  $f_i$  are defined by

$$f_i' = \frac{p_i^*}{p_i} = \frac{p_i^*}{N_i P}, \tag{355}$$

$$f_i = \frac{p_i^* V}{n_i R T}. \tag{356}$$

The values of  $1 - f_i'$  or  $1 - f_i$  and of  $\log f_i'$  or  $\log f_i$  are all measures of deviation from perfection.

Thermodynamics can by itself predict nothing concerning the extent to which any gaseous mixture will differ from a perfect

gaseous mixture. Statistical mechanics, however, predicts that at pressures where the deviations from perfection are small the Helmholtz free energy  $F$  of an imperfect gaseous mixture will be of the form

$$F = \sum_i n_i F_i^\circ(T) + \sum_i n_i RT \log \frac{n_i}{V} - \sum_{i,k} \frac{B_{i,k} \cdot n_i \cdot n_k}{\sigma_{i,k} \cdot V}, \quad (357)$$

where  $F_i^\circ$  and  $B_{i,k}$  depend on the temperature only.  $\sigma_{i,k}$  is merely a symmetry number, being equal to unity except in the case  $i = k$ , when it has the value 2. If it were omitted it would be necessary to assign to the symmetrical  $B_{i,i}$  values halved relatively to the unsymmetrical  $B_{i,k}$ .

From (357) we deduce, by means of (27.2), the formula for the total pressure

$$\begin{aligned} P &= - \left( \frac{\partial F}{\partial V} \right)_{T, n_i} \\ &= \sum_i n_i \frac{RT}{V} - \sum_{i,k} \frac{B_{i,k}}{\sigma_{i,k}} \cdot \frac{n_i}{V} \cdot \frac{n_k}{V}. \end{aligned} \quad (358)$$

According to the definition (318) of the partial vapour pressure, we obtain from (358)

$$p_i = n_i \frac{RT}{V} - N_i \sum_{i,k} \frac{B_{i,k}}{\sigma_{i,k}} \cdot \frac{n_i}{V} \cdot \frac{n_k}{V}. \quad (359)$$

From (357) we deduce, by means of (27.3), for the chemical potential of the species  $i$

$$\begin{aligned} \mu_i &= \left( \frac{\partial F}{\partial n_i} \right)_{T, V, n_j} \\ &= F_i^\circ(T) + RT + RT \log \frac{n_i}{V} - \sum_k B_{i,k} \cdot \frac{n_k}{V}. \end{aligned} \quad (360)$$

Comparing (360) with (353), we obtain for the fugacity  $p_i^*$  of the species  $i$

$$RT \log p_i^* = RT \log \frac{n_i RT}{V} - \sum_k B_{i,k} \cdot \frac{n_k}{V}. \quad (361)$$

From (361) and (356) we obtain directly for the second kind of activity coefficient  $f_i$

$$\log f_i = - \frac{1}{RT} \sum_k B_{i,k} \cdot \frac{n_k}{V}. \quad (362)$$



For the first kind of activity coefficient  $f_i'$  we have, according to (361), (359) and (355),

$$\begin{aligned}\log f_i' &= \log \frac{p_i^* V}{n_i RT} - \log \frac{p_i V}{n_i RT} \\ &= -\frac{1}{RT} \sum_k B_{i,k} \cdot \frac{n_k}{V} - \log \left\{ 1 - \sum_k \frac{n_k}{V} \cdot \sum_{l,k} \frac{B_{l,k}}{\sigma_{l,k}} \cdot \frac{N_l N_k}{RT} \right\}, \quad (363)\end{aligned}$$

or expanding the last logarithm and neglecting, compared with unity, terms of the second order of smallness

$$\log f_i' = -\frac{1}{RT} \sum_k B_{i,k} \cdot \frac{n_k}{V} + \frac{\sum_k n_k}{V} \cdot \sum_{l,k} \frac{B_{l,k}}{\sigma_{l,k}} \cdot \frac{N_l N_k}{RT}. \quad (364)$$

If we accept (358) as the equation of state for slightly\*imperfect gaseous mixtures,  $f_i$  is a considerably simpler function of the concentrations than  $f_i'$  and is therefore to be chosen for preference as the "activity coefficient".

*Temperature Coefficient of Fugacities and of Activity Coefficients.*  
—In terms of fugacities the general formula (173)

$$\left( \frac{\partial \mu_i / T}{\partial T} \right)_{P, n_i, n_j} = -\frac{H_i}{T^2}, \quad (365)$$

becomes

$$\frac{d\mu_i^\circ / T}{dT} + R \left( \frac{\partial \log p_i^*}{\partial T} \right)_{P, n_i, n_j} = -\frac{H_i}{T^2}. \quad (366)$$

But in the limit of low pressures  $p_i^*$  becomes simply the partial vapour pressure  $p_i$ , so that the second term vanishes in (366) which then becomes

$$\frac{d\mu_i^\circ / T}{dT} = -\frac{H_i^\circ}{T^2}, \quad (367)$$

where  $H_i^\circ$  is the value of  $H_i$  at pressures so low that the gas is perfect. Subtracting (367) from (366), we obtain

$$\left( \frac{\partial \log p_i^*}{\partial T} \right)_{P, n_k} = -\frac{H_i - H_i^\circ}{RT^2}. \quad (368)$$

The temperature coefficient of the activity coefficients  $f_i'$  of the first kind is at once obtained from (368) by substituting from (355)

$$p_i^* = p_i f_i' = N_i P f_i'. \quad (369)$$

We obtain

$$\left(\frac{\partial \log f_i'}{\partial T}\right)_{P, n_i, n_j} = -\frac{H_i - H_i^\circ}{RT^2}. \quad (370)$$

A simple physical significance can be assigned to the quantity  $H_i^\circ - H_i$  in connection with the Joule-Thomson effect. Suppose the gaseous mixture at the given pressure  $P$  be forced through a plug, the pressure on the other side being so low that the gas becomes perfect. In order that the temperature of the gas on passing through the plug may remain unaltered, heat must be supplied to it of amount  $H_i^\circ - H_i$  for each mole of each species  $i$  passing through the plug.

*Equilibria of Imperfect Gases.*—The usefulness of the functions called the fugacities of the components of a mixture of imperfect gases is that all equilibrium conditions involving these gases can be very simply expressed in terms of the fugacities, whose values are deducible from a knowledge of the equation of state, and so are independent of what equilibrium is being considered.

For the case of two gaseous mixtures,  $\alpha$  and  $\beta$ , at the same temperature separated by a membrane permeable to some of the species but impermeable to others, we have the equilibrium conditions

$$\mu_i^\alpha = \mu_i^\beta, \quad (371)$$

for all species  $i$  to which the membrane is permeable, the indices  $\alpha$  and  $\beta$  referring to the two phases. According to (353) we may express (371) in terms of fugacities in the form

$$[RT \log p_i^*]^\alpha = [RT \log p_i^*]^\beta, \quad (372)$$

or simply

$$[p_i^*]^\alpha = [p_i^*]^\beta. \quad (373)$$

Thus the condition for equilibrium between two gaseous mixtures as regards the species  $i$  is that this species should have the same fugacity in the two mixtures. As regards this property the fugacity of an imperfect gas plays the same part as the partial vapour pressure of a perfect gas.

For the chemical equilibrium

$$lL + mM = qQ + rR, \quad (374)$$

between imperfect gases, we can, in exact analogy with the deduction of the equilibrium condition (341) for perfect gases, deduce the equilibrium condition

$$\frac{(p_Q^*)^q \cdot (p_R^*)^r}{(p_L^*)^l \cdot (p_M^*)^m} = K(T), \quad (375)$$

where the equilibrium constant  $K(T)$  depends only on the temperature.

For the temperature coefficient of  $K$  we obtain in exact analogy with (348), by using (322),

$$\frac{d \log K}{dT} = \frac{I_p^\circ}{RT^2}, \quad (376)$$

where  $I_p^\circ$  is the heat of reaction, not in the actual gaseous mixture, but at such a low pressure that the gases have become perfect.

#### NOTES AND REFERENCES

*Partial Vapour Pressures.*—The definition of partial vapour pressure chosen is that of Lewis and Randall. The total pressure of a mixture of gases is then by definition equal to the sum of the partial pressures of the components, whether the gases be perfect or not.

*Equation of State of Imperfect Gaseous Mixtures.*—The only statistical mechanical discussion of imperfect gases that is altogether sound is given in Fowler's "Statistical Mechanics".

*Fugacity and Activity Coefficients.*—These functions are due to G. N. Lewis, and were first defined in *Proc. Am. Acad.*, **37**, 49 (1901), and *Z. Physikal. Chem.*, **38**, 205 (1901).

## CHAPTER V

### CONDENSED PHASES OF SEVERAL COMPONENTS

#### *Relation between Chemical Potentials and Partial Vapour Fugacities.*

—The formulæ derived in the last chapter for gaseous mixtures have an importance extending beyond their application to the systems for which they were derived. For the chemical potential of each component has the same value in any two phases in equilibrium as regards this component. Hence the chemical potential  $\mu_i$  of a species  $i$  in any condensed phase is given by

$$\mu_i = \mu_i^\circ(T) + RT \log p_i^*, \quad (377)$$

where  $\mu_i^\circ$  depends only on the temperature, being the same in all phases, and  $p_i^*$  is the “partial vapour fugacity” of  $i$ , that is to say, the fugacity of  $i$  in the saturated vapour in equilibrium with the condensed phase.

If the saturated vapour in equilibrium with the condensed phase behaves as a perfect gas, (377) becomes

$$\mu_i = \mu_i^\circ(T) + RT \log p_i. \quad (378)$$

$\mu_i$  here denotes the chemical potential either in the condensed phase or in the saturated vapour phase,  $\mu_i^\circ$  depends only on the temperature, and  $p_i$  is the partial vapour pressure of  $i$ . As long as the temperature is sufficiently below the critical temperature, the saturated vapour will usually approximate fairly closely to a perfect gas. In treating condensed phases we shall therefore assume (378) to be of general validity, with the reservation that if the vapour should not be a perfect gas,  $p_i$  must be taken to denote the fugacity instead of the partial vapour pressure.

From (378) we make the important deduction that in any formula that does not involve a temperature variation we may always make the substitutions

$$d\mu_i = RT d \log p_i, \quad (379)$$

and

$$\Delta\mu_i = RT \Delta \log p_i, \quad (380)$$

where the operator  $\Delta$  denotes the difference between the values in two phases at the same temperature.

*Heterogeneous Equilibrium.*—In accordance with (378) the general condition (82) for equilibrium between two phases  $\alpha$  and  $\beta$  as regards the species  $i$

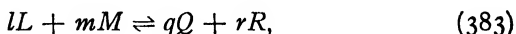
$$\mu_i^\alpha = \mu_i^\beta, \quad (381)$$

becomes

$$p_i^\alpha = p_i^\beta. \quad (382)$$

This means that  $i$  has the same partial vapour pressure in two phases in equilibrium as regards  $i$ , a condition that is physically obvious. In discussing heterogeneous equilibria at a given temperature, we may use (381) or (382) indiscriminately as alternative equilibrium conditions.

*Homogeneous Chemical Equilibrium.*—For homogeneous equilibrium in any phase we may for the reaction



replace the general condition (97) by (341)

$$\frac{(p_Q)^q \cdot (p_R)^r}{(p_L)^l \cdot (p_M)^m} = K(T), \quad (384)$$

where  $p_L, p_M, p_Q, p_R$  denote the partial vapour pressures of  $L, M, Q, R$  in the vapour in equilibrium with the given phase, and  $K(T)$  is a function of the temperature only.

*Duhem-Margules Relation.*—If we substitute from (379) in the general formula (32) applied to variations at constant temperature, we obtain

$$dT = 0 \quad VdP - \sum_i n_i RT d \log p_i = 0, \quad (385)$$

with the important special case when the total pressure  $P$  is kept constant

$$dT = 0 \quad dP = 0 \quad \sum_i n_i d \log p_i = 0, \quad (386)$$

or dividing by  $\sum_k n_k$

$$dT = 0 \quad dP = 0 \quad \sum_i N_i d \log p_i = 0. \quad (387)$$

This relation between the variations with composition of the partial vapour pressures of the components, at constant temperature and pressure, is known as the Duhem-Margules relation.

*Mixtures with Maximum Vapour Pressure and Minimum Boiling-point and with Minimum Vapour Pressure and Maximum Boiling-point.*—Let us consider a liquid mixture  $L$  in equilibrium with the vapour phase  $G$ . For variations of composition of the

two phases we have, according to (32) applied to a quantity of each phase containing altogether one mole

$$-S^L dT + V^L dP - \sum_i N_i^L d\mu_i^L = 0, \quad (388)$$

$$-S^G dT + V^G dP - \sum_i N_i^G d\mu_i^G = 0. \quad (389)$$

If these variations are consistent with the maintenance of equilibrium between the two phases, we have, according to (82), for each species  $i$

$$d\mu_i^L = d\mu_i^G. \quad (390)$$

Now, suppose the relative compositions of the liquid and vapour phases in equilibrium should happen to be identical, that is to say, that for each species  $i$

$$N_i^L = N_i^G. \quad (391)$$

Then, using (390) and (391), and subtracting (388) from (389), we obtain

$$(S^G - S^L)dT - (V^G - V^L)dP = 0. \quad (392)$$

If now we consider such variations of composition at constant temperature, so that

$$dT = 0, \quad (393)$$

it follows from (392) that

$$(V^G - V^L)dP = 0, \quad (394)$$

or, since

$$V^G \neq V^L, \quad (395)$$

that

$$dP = 0. \quad (396)$$

If, on the other hand, we consider variations at constant pressure, so that

$$dP = 0, \quad (397)$$

it follows from (392) that

$$(S^G - S^L)dT = 0, \quad (398)$$

or, since

$$S^G \neq S^L, \quad (399)$$

that

$$dT = 0. \quad (400)$$

Formulae (396) and (400) tell us that whenever the compositions expressed in mole fractions of the liquid and vapour phases in mutual equilibrium are identical the equilibrium pressure (total vapour pressure) at given temperature is a maximum or minimum, and the equilibrium temperature (boiling-point) at given pressure is a minimum or maximum. An example of this is illustrated for the case of a two-component system in Fig. 5, in which the boiling-point is plotted against the composition of the liquid phase in the lower curve and the composition of the vapour phase in the upper curve. For instance, the points  $L$  and  $V$  represent the liquid and vapour phases in equilibrium at one temperature;  $L'$ ,  $V'$  is another such pair, and  $L''$ ,  $V''$  a third. The point  $M$

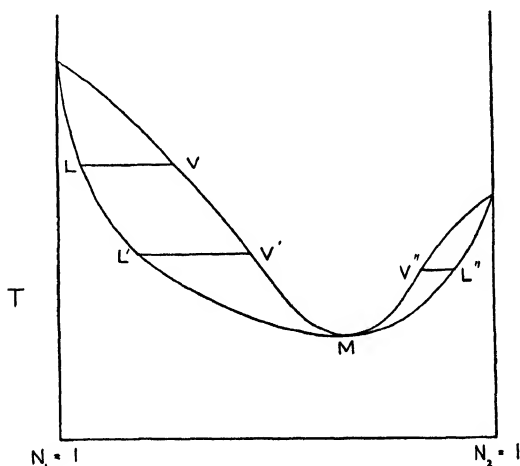


FIG. 5.

represents liquid and vapour of the same composition, expressed in mole fractions, in equilibrium and in this case the equilibrium temperature (boiling-point) is a minimum.

*Dependence of Vapour Pressure on External Pressure.*—From (378) and (153) we deduce the fact that the partial vapour pressure  $p_i$  of a component  $i$  in a condensed phase of given composition varies not only with the temperature, but also with the total pressure on the phase. The relation is

$$RT \left( \frac{\partial \log p_i}{\partial P} \right)_{T, n_i, n_j} = \left( \frac{\partial \mu_i}{\partial P} \right)_{T, n_i, n_j} = V_i. \quad (401)$$

where  $V_i$  is the partial molar volume in the condensed phase.

In theory the total pressure on a condensed phase, at a given

temperature in equilibrium with saturated vapour, may be varied by separating it from the vapour by a piston permeable to the vapour but not to the liquid. In practice an analogous result is obtained by addition to the vapour phase of an inert gas insoluble in the condensed phase. This inert gas may then be regarded, not as a component of the system, but merely as part of the apparatus used to fix the pressure on the liquid phase.

*Solutions, Solvent and Solute.*—A homogeneous phase of more than one component is called a solution. This term is most usually applied to liquid phases, but this restriction is not essential. In the case of a gaseous phase it is more usual to speak of a gaseous mixture than a gaseous solution. The thermodynamic treatment of gaseous mixtures was given in the previous chapter. Solid solutions are less common than liquid solutions, but from a thermodynamic point of view analogous. It will be convenient to treat in detail only liquid solutions. It will be obvious how a similar treatment could be applied to solid solutions.

It is usual to denote one of the components of a solution as the "solvent" and to call all the remaining components the "solute" species. From a thermodynamic point of view there is no distinction between solvent and solute, and it is quite arbitrary which species is regarded as solvent. In practice, it is usual to designate by the term solvent that species present in greatest proportion in the solution which in the pure form exists in the liquid state at the temperature and pressure of the solution, or at least at temperatures and pressures not far removed from those of the solution.

We shall always denote the solvent species by the suffix 0 and the solute species by the suffix  $S$ . According to the definition (98) of the mole fractions, we have the identity

$$N_0 + \sum_s N_s = 1. \quad (402)$$

*Independent Variables Describing Composition.*—It is convenient to regard the mole fractions  $N_s$  of the various solute species as independent variables, and the mole fraction  $N_0$  of the solvent as being defined by

$$N_0 = 1 - \sum_s N_s, \quad (403)$$

so that

$$\frac{\partial N_0}{\partial N_s} = -1. \quad (404)$$

Since the value of any intensity factor (intensive property)  $I$  of a solution does not depend on the quantity of the solution, but



only on the temperature, pressure and composition, we have for its most general variation

$$dI = \left(\frac{\partial I}{\partial T}\right)_{P, N_s} dT + \left(\frac{\partial I}{\partial P}\right)_{T, N_s} dP + \sum_s \left(\frac{\partial I}{\partial N_s}\right)_{T, P} dN_s. \quad (405)$$

As we shall always choose  $T$ ,  $P$ ,  $N_s$  as independent variables, we may write (405) more shortly

$$dI = \frac{\partial I}{\partial T} dT + \frac{\partial I}{\partial P} dP + \sum_s \frac{\partial I}{\partial N_s} dN_s. \quad (406)$$

As the last sum on the right of (406) will occur repeatedly, it is convenient to use a further abbreviation defined by

$$DI \equiv \sum_s \frac{\partial I}{\partial N_s} dN_s. \quad (407)$$

$DI$  thus denotes any infinitesimal change in  $I$  due to an infinitesimal change of composition at constant temperature and constant pressure. Using the shorthand notation defined by (407), (406) takes the form

$$dI = \frac{\partial I}{\partial T} dT + \frac{\partial I}{\partial P} dP + DI. \quad (408)$$

*Osmotic Pressure.*—Suppose we have two liquid solutions at the same temperature separated by a membrane permeable only to the one solvent species and impermeable to all the solute species. The condition that the two liquid phases should be in equilibrium as regards the solvent species (denoted by the suffix  $o$ ) is, according to (381)

$$\mu_o^\alpha = \mu_o^\beta, \quad (409)$$

where the indices  $\alpha$  and  $\beta$  refer to the two phases. Alternatively, we may, according to (382), take as the condition of osmotic equilibrium

$$p_o^\alpha = p_o^\beta. \quad (410)$$

This membrane equilibrium as regards the solvent is called "osmotic" equilibrium.

Suppose, now, that the composition and pressure of the phase  $\beta$  be kept constant, while those of the phase  $\alpha$  be changed in such a manner that osmotic equilibrium is maintained. The condition for this is that in phase  $\alpha$

$$d\mu_o^\alpha = 0 \quad (411)$$

or alternatively

$$d \log p_0^\alpha = 0. \quad (412)$$

This last condition may be written more fully in the abbreviated notation of (408),

$$\frac{\partial \log p_0^\alpha}{\partial P} dP^\alpha + D \log p_0^\alpha = 0, \quad (413)$$

or according to (401),

$$\frac{V_0^\alpha}{RT} dP^\alpha + D \log p_0^\alpha = 0. \quad (414)$$

As the composition of the phase  $\alpha$  is varied, that of phase  $\beta$  being kept constant, the pressure on phase  $\alpha$  must also be altered to maintain osmotic equilibrium with phase  $\beta$  kept at constant pressure. Thus, in general, for the two phases separated by the semi-permeable membrane to be in equilibrium as regards the solvent (osmotic equilibrium) the pressures of the two phases will have to be different.

In the particular case that phase  $\beta$  is simply the pure solvent the excess pressure on the solution (phase  $\alpha$ ) over that on the pure solvent (phase  $\beta$ ) is called the "osmotic pressure" of the solution, and will be denoted by  $\Pi$ . Thus, at osmotic equilibrium

$$\Pi = P^\alpha - P^\beta. \quad (415)$$

If we imagine the pressure  $P^\beta$  on the pure solvent kept constant at the value  $P^0$  (say 1 atmosphere), and the composition of the solution and its pressure varied simultaneously in such a way as to maintain osmotic equilibrium, we have

$$d\Pi = dP^\alpha. \quad (416)$$

Substituting for  $dP^\alpha$  in (414) the value given by (416), we obtain

$$\frac{V_0}{RT} d\Pi = -D \log p_0. \quad (417)$$

This equation expresses the condition that the fractional alteration  $D \log p_0$  of the vapour pressure of the solvent due to a change of composition can be just counteracted by a simultaneous alteration of the external pressure by an amount  $d\Pi$ . The actual value of the osmotic pressure of the solution is obtained by integrating (417) through a range of composition extending from pure solvent when

$$P^\beta = P^\alpha = P^0 \quad \Pi = 0 \quad (418)$$

to the actual solution. We thus obtain

$$\frac{1}{RT} \int_{P^0}^{P^0 + \Pi} V_0 dP = - \int_{N_S=0}^{N_S} D \log p_0 = \log \frac{p_0^0}{p_0}, \quad (419)$$

where  $p_0$  and  $p_0^0$  denote the vapour pressure of the solvent in the solution and in the pure state, both at the external pressure  $P^0$ . Formula (419) is exact, provided only that the vapour phase behaves as a perfect gas. Even if this condition is not fulfilled (419) will still be exact if  $p_0$  and  $p_0^0$  represent fugacities instead of vapour pressures. The relation (419) is contained implicitly in Gibbs' writings, but was first given explicitly in an accurate form by Porter.

From the form of (419) it appears that the osmotic pressure  $\Pi$  depends on the pressure  $P^0$  on the pure solvent. This is strictly true, but as long as the pressure  $P^0$  on the solvent is not too great its value is irrelevant. That this is the case is very simply shown by considering variations of the osmotic equilibrium between the solution  $\alpha$  and the pure solvent  $\beta$ , keeping the composition of the solution constant but varying the pressures  $P^\alpha$  and  $P^\beta$  on both phases. The condition for maintenance of osmotic equilibrium is then

$$\frac{\partial \mu_0^\alpha}{\partial P} dP^\alpha = \frac{\partial \mu_0^\beta}{\partial P} dP^\beta, \quad (420)$$

or alternatively

$$\frac{\partial \log p_0^\alpha}{\partial P} dP^\alpha = \frac{\partial \log p_0^\beta}{\partial P} dP^\beta. \quad (421)$$

Substituting from (153) into (420) or from (401) into (421) we obtain

$$V_0^\alpha dP^\alpha = V_0^\beta dP^\beta. \quad (422)$$

Substituting (415) into (422), and writing  $P^0$  instead of  $P^\beta$ , we have

$$V_0^\alpha (d\Pi + dP^0) = V_0^\beta dP^0. \quad (423)$$

From this we deduce

$$\frac{\partial \Pi}{\partial P_0} = \frac{V_0^\beta - V_0^\alpha}{V_0^\alpha}. \quad (424)$$

As the difference between the partial molar volume of the solvent in the phases  $\alpha$  (solution) and  $\beta$  (pure solvent) will generally be very small compared with its actual value  $V_0^\alpha$  or  $V_0^\beta$  in either

phase, it follows from (424) that  $\Pi$  will be practically independent of  $P^\circ$ .

It is therefore justifiable to define the osmotic pressure  $\Pi$  as the pressure on the solution when in osmotic equilibrium with the pure solvent at *zero* pressure, but to measure it as the excess pressure on the solution when in osmotic equilibrium with the pure solvent at *atmospheric* pressure. We are thus justified in replacing (419) by the simpler relation

$$\int_0^\Pi v_0 d\Pi = RT \log \frac{p_0^\circ}{p_0}, \quad (425)$$

where  $p_0$  and  $p_0^\circ$  are the vapour pressures of the solvent in the solution and in the pure state, both at the same external pressure, but it is of no significance whether we take this external pressure to be zero or atmospheric or an intermediate value.

*Pressure on Semi-permeable Membrane.*—The osmotic pressure is by definition a pressure that must be applied to the solution to bring it into a certain equilibrium condition. It is not a pressure exerted by the solution or part of the solution at its normal low pressure. It is, in fact, analogous to the freezing-point of a solution, which has no relation to the actual temperature of the solution, but is the temperature to which it must be brought to reach a certain equilibrium state. The osmotic pressure is nevertheless sometimes defined as the pressure exerted on a membrane, permeable only to the solvent, separating the solution from pure solvent. This definition, unless carefully qualified, is incorrect. Another definition sometimes given is the pressure exerted by the solute molecules on a membrane permeable only to the solvent. This definition is still more incorrect than the last. Although we wish so far as possible to exclude considerations of a non-thermodynamic nature from our treatment, we shall in the present case depart from our rule. The confused ideas generally prevalent concerning the pressure exerted on a semi-permeable membrane seem to us to justify our inclusion of a kinetic discussion of this phenomenon.

Let us first consider the pure solvent at a given pressure. The pressure exerted by the liquid on the walls of the containing vessel may be considered as due to the momentum transferred to the wall when molecules are reflected there. Its value is, in fact, in appropriate units, equal to the product of the number of molecules reflected per unit time and the mean momentum transferred to the wall in such a reflection. Suppose now one of the walls replaced by a wall "permeable to the solvent". This, of course, does not mean that the wall offers no resistance at all to

the flow of solvent. On the contrary, it means in all practical cases that a certain quite *small fraction* of the molecules striking the wall, pass through. This fraction depends on the degree of porosity of the semi-permeable wall. The momentum transferred to the wall in unit time will be less than in the case of a non-permeable wall by the amount of momentum of the molecules passing through in unit time. If we denote by  $P$  the pressure of the liquid on the non-permeable wall, we may denote the pressure on the permeable wall by  $P(1 - \alpha)$  where  $\alpha$  is a certain small fraction depending on the porosity of the membrane, and possibly also on the value of  $P$  itself.

Now, let us consider a solution at a given pressure  $P'$ . This pressure may be considered as due partly to the transfer of momentum of the solvent molecules to the walls and partly to the transfer of momentum of the solute molecules. We may therefore write formally

$$P' = P_0' + P_s', \quad (426)$$

where  $P_0'$  and  $P_s'$  respectively denote the contributions of the solvent and the solute molecules to the pressure. If, now, one of the walls be permeable to the solvent, the part of the pressure due to the solvent molecules will be reduced by a small fraction  $\alpha'$ , so that we have

$$P' = P_0'(1 - \alpha') + P_s'. \quad (427)$$

Let us now consider a membrane permeable to the solvent but not to the solute separating the pure solvent at the pressure  $P$  and the solution at the pressure  $P'$ . Then the resultant pressure  $P_M$  on the membrane tending to make it move towards the side of pure solvent, or alternatively the external pressure that must be applied to it to prevent it from moving towards the side of the pure solvent, is given by

$$P_M = P_0'(1 - \alpha') + P_s' - P(1 - \alpha). \quad (428)$$

If the total pressure of the solution  $P'$  is equal to the total pressure  $P$  of the pure solvent, e.g. both at one atmosphere, we have the condition

$$P_0' + P_s' = P, \quad (429)$$

but this condition does not enable us to evaluate  $P_M$ , nor even to determine its sign. This means that it is thermodynamically possible that the membrane may tend to move towards the side of pure solvent. This does not mean that the solution tends to become more concentrated. For it must be remembered that

owing to the greater concentration of solvent on the side of pure solvent, more solvent will pass through the membrane from this side to that of the solution than in the opposite direction. There will thus be a resultant stream of solvent from the side of the pure solvent to that of the solution. Although we cannot evaluate  $P_M$ , or even predict its sign in general, it is perhaps not without interest to investigate its value under certain extremely idealised conditions. Imagine the solvent and solute molecules identical in all respects except as regards their ability to pass through the membrane. We may then write

$$P_0' = N_0 P' = N_0 P, \quad (430\cdot1)$$

$$P_S' = N_S P' = N_S P, \quad (430\cdot2)$$

where  $N_0$ ,  $N_S$  are the mole fractions of solvent and solute respectively. We may also assume

$$\alpha = \alpha'. \quad (431)$$

Under these idealised conditions we have

$$\begin{aligned} P_M &= P N_0(1 - \alpha) + P N_S - P(1 - \alpha) \\ &= P N_S \alpha. \end{aligned} \quad (432)$$

If we take the pressure of the solvent and solution separated by the membrane to be one atmosphere, the mole fraction of solute to be 0.01 (as in a half molar aqueous solution) and  $\alpha$  to have the improbably high value 0.1, we find that  $P_M$  is of the order of magnitude 0.001 atmospheres, that is practically negligible. On the other hand, the value of the osmotic pressure  $\Pi$  of a half molar aqueous solution is of the order of magnitude of 10 atmospheres.

If we now consider the total pressure  $P'$  of the solution to be not equal to, but greater than, that of the pure solvent, then both  $P_0'$  and  $P_S'$  will be increased. The increase of these pressures will counterbalance the smaller concentration of solvent on the side of the solution, and at a sufficient increase in their values the quantities of solvent passing through the membrane in the two opposite directions will be equal. Under these conditions there is osmotic equilibrium, and the resultant pressure  $P_M$  on the membrane is now equal to the osmotic pressure  $\Pi$ .

To sum up. When the solution is at the same pressure (atmospheric) as the solvent, there will be a resultant flow of solvent through the membrane from the solvent to the solution, but the resultant pressure on the membrane itself is negligibly small, and may be in either direction. If, however, the solution is subjected to a certain high external pressure, the flow of solvent

through the membrane is equal in either direction ; there is then osmotic equilibrium and the excess pressure on the solution over the pressure (atmospheric) of the solvent is by definition the osmotic pressure. Under conditions of osmotic equilibrium, but only under these conditions, is the external pressure required to prevent the membrane from moving equal to the osmotic pressure.

*Equilibrium between Solution and Pure Solid Phase.*—The condition for equilibrium as regards the species  $i$  between a solution, containing  $i$  either as solvent or solute, and the solid phase of pure  $i$  may be written

$$\mu_i' = \mu_i, \quad (433)$$

where the dashed symbol refers to the solid phase and the undashed to the solution. For variations of temperature, pressure and composition consistent with the maintenance of equilibrium, we have

$$d\mu_i' = d\mu_i, \quad (434)$$

or using (408), (152) and (153)

$$-S_i'dT + V_i'dP = -S_i dT + V_i dP + D\mu_i. \quad (435)$$

If the composition of the solution be kept constant, and the pressures on the two phases are the same, (435) becomes

$$(S_i - S_i')dT = (V_i - V_i')dP, \quad (436)$$

or

$$\frac{dT}{dP} = \frac{V_i - V_i'}{S_i - S_i'}. \quad (437)$$

Since according to (25) and (30.6)

$$TS_i = H_i - \mu_i, \quad (438.1)$$

$$TS_i' = H_i' - \mu_i', \quad (438.2)$$

and we have the equilibrium condition (433), we may instead of (437) write

$$\frac{dT}{dP} = \frac{(V_i - V_i')T}{H_i - H_i'}, \quad (439)$$

or

$$\frac{dT}{dP} = \frac{(V_i - V_i')T}{L_i}, \quad (440)$$

where  $L_i$  is the "heat of solution" of  $i$  in the solution, that is the heat absorbed when one mole of the solid phase of  $i$  dissolves in a large quantity of the solution at the temperature and pressure at which the solid and solution are in equilibrium. It is to be noticed that (440) is of identically the same form as (273), which may be regarded as the special case of (440) for a liquid phase consisting of the pure species  $i$ .

A more important application of (435) is to variations of the composition of the solution and the dependence thereon of the equilibrium temperature, both phases being kept at the same constant pressure. In this case (435) simplifies to

$$(S_i - S_i')dT = D\mu_i, \quad (441)$$

or using (438) and (433),

$$\frac{H_i - H_i'}{T}dT = D\mu_i, \quad (442)$$

or introducing  $L_i$  the heat of solution of the pure solid species  $i$  into the solution in equilibrium with the pure solid phase

$$\frac{L_i}{T}dT = D\mu_i. \quad (443)$$

In the special case that the species  $i$  is the only solute species  $s$ , (443) may be written

$$\frac{L_s}{T}dT = \frac{\partial \mu_s}{\partial N_s}dN_s, \quad (444)$$

or

$$\frac{dN_s}{dT} = \frac{L_s}{T} \left/ \frac{\partial \mu_s}{\partial N_s} \right. \quad (445)$$

This formula expresses the dependence on the temperature of the composition of the solution saturated with  $s$ , in other words, the dependence on the temperature of the solubility of  $s$  in terms of  $L_s$ , the heat of solution of  $s$  into the saturated solution.

If, on the other hand, the species  $i$  is the solvent species  $0$  (443) may be written

$$\frac{L_0}{T}dT = D\mu_0, \quad (446)$$

and it is customary to use a different terminology; (446) is said to express the dependence of the "freezing-point"  $T$  on the composition of the solution.  $L_0$  is in this case called the "heat of fusion" of the solvent.



*Boiling-point of Solution.*—If the components of the solution other than the solvent itself are all non-volatile, the boiling-point of the solution is the temperature at which it is in equilibrium with the solvent vapour at a given pressure, usually one atmosphere. If we use dashed symbols to refer to the vapour phase and undashed symbols to refer to the liquid phase, we have the equilibrium condition

$$\mu_0' = \mu_0. \quad (447)$$

For variations of temperature and composition consistent with maintenance of equilibrium at constant pressure (usually atmospheric), we have

$$d\mu_0' = d\mu_0, \quad (448)$$

or using (408) and (152)

$$-S_0'dT = -S_0dT + D\mu_0. \quad (449)$$

But, according to (25) and (30.6), we have

$$TS_0 = H_0 - \mu_0, \quad (450.1)$$

$$TS_0' = H_0' - \mu_0', \quad (450.2)$$

and so using the equilibrium condition (447), we may rewrite (449) as

$$\frac{H_0 - H_0'}{T}dT = D\mu_0, \quad (451)$$

or

$$-\frac{L_0}{T}dT = D\mu_0, \quad (452)$$

where  $L_0$  is the latent heat of evaporation of the solvent from the solution to the vapour in equilibrium with it.

## NOTES AND REFERENCES

*Osmotic Pressure.*—The first completely satisfactory thermodynamic treatment of osmotic pressure was given by Porter in *Proc. Roy. Soc.*, **79**, 519 (1907), and **80**, 457 (1908). A simpler derivation of the same relations, together with a clear explanation of the physical significance of osmotic pressure, was given by Callendar in *Proc. Roy. Soc.*, **80**, 476, 483 (1908).

*Pressure on Semi-permeable Membrane.*—The distinction between osmotic pressure and the pressure on a semi-permeable membrane is clearly emphasised by Washburn in "Principles of Physical Chemistry" (1921). The detailed discussion given in this chapter has not previously been published. It was contained in a thesis written by the author in 1927.

## CHAPTER VI

### IDEAL SOLUTIONS

*Chemical Potential as Function of Temperature, Pressure and Composition.*—The formulæ of the previous chapter show how all the equilibrium properties of a solution can be expressed in terms of the chemical potentials of its components. All these equilibrium properties will therefore be completely determined if we can express the chemical potentials as functions of the temperature, pressure and mole fractions of the solution. Thermodynamic considerations, of course, cannot alone predict the form of this functional relationship, but only impose the restriction (33),

$$\sum_i N_i d\mu_i = 0, \text{ when } dT = 0, dP = 0, \quad (453)$$

relating the changes with composition of the various components at given temperature and pressure. Now the mole fractions  $N_i$  are connected by the identical relation (99)

$$\sum_i N_i = 1. \quad (454)$$

From this we deduce

$$\sum_i dN_i = 0, \quad (455)$$

or

$$\sum_i N_i d \log N_i = 0. \quad (456)$$

Comparison of (453) and (456) shows that a thermodynamically allowable form for  $\mu_i$  is

$$\mu_i = A + B \log N_i. \quad (457)$$

where  $A$  and  $B$  may depend on the temperature and pressure but not on the composition. As a matter of fact, it can be shown by statistical mechanical considerations that for solutions so

dilute that the interaction between the solute molecules is negligible, the chemical potential is of the type (457) and  $B$  has the value  $RT$ , that is to say

$$\mu_i = \mu_i^\circ + RT \log N_i, \quad (458)$$

where  $\mu_i^\circ$  depends on the temperature and pressure, but not on the composition. Solutions obeying this law are called "ideal" solutions.

A comparison of (458) with (321) shows that in an ideal solution at given temperature and pressure the chemical potential of each species depends on its mole fraction in precisely the same manner as it does in a mixture of perfect gases at constant temperature and total pressure. The dependence of the chemical potentials on the pressure is, however, as we shall see, entirely different in the two cases.

Thermodynamics can, of course, tell us nothing as to the conditions under which solutions are ideal. Statistical mechanical considerations predict that all solutions tend to become ideal at high dilution, but deviations from ideality may occur as soon as the mole fractions of the solute species are not negligible compared with unity. For solutions of non-electrolytes deviations of the order of 1 per cent. are generally not encountered until the mole fraction of solute is about 0.001. On the other hand, solutions do exist for which deviations from ideality are undetectable throughout the whole range of concentrations. These are, however, exceptional cases, occurring only when solvent and solute are chemically very similar as, for example, mixtures of bromo-benzene and chloro-benzene. Such solutions are called "perfect solutions". At the other extreme are solutions of electrolytes for which deviations from ideality of the order 1 per cent. occur in water at a mole fraction of about  $10^{-6}$  in the case of uni-univalent electrolytes. In the case of electrolytes of higher valency types or solvents of lower dielectric constant appreciable deviations from ideality occur at still considerably lower concentrations. Although the range of validity of formula (458) for the chemical potentials is so varied, the ideal solution is a convenient standard with which to compare any actual solution. It is therefore important to develop in detail the laws of behaviour deducible from (458). These laws are known as the "laws of ideal solutions".

As regards the form of  $\mu_i^\circ$ , we have, according to (153),

$$\frac{\partial \mu_i}{\partial P} = \frac{\partial \mu_i^\circ}{\partial P} = v_i, \quad (459)$$

and according to (173),

$$\frac{\partial \mu_i / T}{\partial T} = \frac{\partial \mu_i^\circ / T}{\partial T} = -\frac{H_i}{T^2}, \quad (460)$$

As  $\mu_i^\circ$  is by supposition independent of the composition, it follows from (459) and (460) that  $V_i$  and  $H_i$  are also independent of the composition.

*Mixing Properties.*—The volume  $V$  of the whole solution is, according to (119), given by

$$V = \sum_i n_i V_i = \sum_i n_i V_i^\circ, \quad (461.1)$$

where  $V_i^\circ$  is the value of  $V_i$  at infinite dilution. This means that any two ideal solutions in the same solvent will mix at constant temperature and pressure without expansion or contraction. In particular, there will be no contraction or expansion if an ideal solution is diluted by the addition of pure solvent.

Similarly, the heat content  $H$  of the whole solution is, according to (119), given by

$$H = \sum_i n_i H_i = \sum_i n_i H_i^\circ, \quad (461.2)$$

where  $H_i^\circ$  is the value of the partial molar heat content of  $i$  at infinite dilution. This means that any two ideal solutions in the same solvent will mix at constant temperature and pressure without any change in the total heat content, and so without absorption or emission of heat. In particular, if an ideal solution be diluted with pure solvent at constant temperature and pressure, no heat will be absorbed or given out. In other words, the "heat of dilution" is zero.

*Alternative Form for Chemical Potentials.*—We have shown that the partial molar volume  $V_i$  of each species  $i$  is in an ideal solution independent of the composition, and is so a function of the temperature and pressure only. At a given temperature we may therefore, just as for a single component liquid, write

$$V_i = V_i^*(1 - \kappa_i P), \quad (462.1)$$

where  $V_i^*$  is the value of  $V_i$  at zero pressure, and  $\kappa_i$  is a compressibility coefficient which may be taken as independent of the pressure and the composition. Both  $V_i^*$  and  $\kappa_i$  will, of course, depend on the temperature.

For the dependence of the chemical potential  $\mu_i$  of  $i$  on the pressure, we have, according to (153) and (462.1),

$$\frac{\partial \mu_i}{\partial P} = V_i = V_i^*(1 - \kappa_i P). \quad (462.2)$$

Integrating (462.2) at constant temperature, and comparing with (458), we find that  $\mu_i$  must be of the form

$$\mu_i = \mu_i^*(T) + PV_i^*(1 - \frac{1}{2}\kappa_i P) + RT \log N_i, \quad (462.3)$$

where  $\mu_i^*$ ,  $V_i^*$ ,  $\kappa_i$  are independent of the pressure and the composition; their values are determined by the temperature and the solvent.

Formula (462.3) shows clearly the dependence of the chemical potentials  $\mu_i$  on the pressure. It should be compared and contrasted with the corresponding formula (321) for the chemical potentials in a mixture of perfect gases.

It is clear that  $\mu_i^*(T)$  is the value of  $\mu_i^\circ(T, P)$  at zero pressure. It follows, by using (460), that

$$\frac{d\mu_i^*/T}{dT} = -\frac{H_i^*}{T^2}, \quad (462.4)$$

where  $H_i^*$  is the value of  $H_i$  at zero pressure.

*Henry's Law for Vapour Pressure of Solute.*—According to formula (458) the chemical potential of the solute species  $s$  in an ideal solution is of the form

$$\mu_s = \mu_s^\circ + RT \log N_s, \quad (463)$$

where  $\mu_s^\circ$  is independent of the composition. But the chemical potential of any species in a condensed phase is equal to its value in the vapour phase in equilibrium with it. Hence, according to (321), we have also

$$\mu_s = \mu_s^{\circ'} + RT \log p_s. \quad (464)$$

where  $\mu_s^{\circ'}$  is a function of the temperature only and  $p_s$  is the saturated partial vapour pressure of  $S$  in the solution. Comparison of (463) and (464) leads to

$$\log p_s = \log N_s + \log k_s, \quad (465)$$

or

$$p_s = k_s N_s, \quad (466)$$

where  $k_s$  is independent of the composition of the solution. Formula (466) is known as Henry's Law for ideal solutions.

For the dependence of  $k_s$  on the temperature, we have, by (463), (464), (322) and (460)

$$\begin{aligned} \frac{\partial \log k_s}{\partial T} &= \frac{1}{R} \frac{\partial \mu_s^\circ/T}{\partial T} - \frac{1}{R} \frac{\partial \mu_s^{\circ'}/T}{\partial T} \\ &= \frac{-H_s^\circ + H_s^{\circ'}}{RT^2} \\ &= \frac{L_s}{RT^2}, \end{aligned} \quad (467)$$

where  $H_s^{\circ'}$  is the partial molar heat content of  $s$  in the vapour phase, and  $L_s$  is the molar latent heat of evaporation of  $s$  from the solution to the vapour in equilibrium with it.

The value of  $k_s$  depends not only on the temperature, but also to some extent on the pressure on the solution. According to (401) and (466) we have

$$\frac{\partial \log k_s}{\partial P} = \frac{V_s^{\circ}}{RT} \quad (468)$$

*Raoult's Law for Vapour Pressure of Solvent.*—Exactly the same derivation of Henry's Law (466) for the solute, applied to the solvent species, denoted by the suffix 0, leads to

$$p_0 = k_0 N_0. \quad (469)$$

But if solutions of given solutes in a given solvent are ideal in any range of finite concentration, they are so *a fortiori* at infinite dilution. But in the limit of infinite dilution  $N_0$  the mole fraction of the solvent becomes unity, and so

$$k_0 = p_0^{\circ}, \quad (470)$$

where  $p_0^{\circ}$  is the vapour pressure of the pure solvent at the given temperature and pressure. (469) therefore becomes

$$p_0 = p_0^{\circ} N_0. \quad (471)$$

This is known as Raoult's Law for ideal solutions.  $p_0^{\circ}$ , of course, depends on the temperature and external pressure on the liquid phase according to formulæ (277) and (314).

*Derivation of Raoult's Law from Henry's Law.*—We have chosen formula (458) for the chemical potentials of both solvent and solute as our definition of an ideal solution. An alternative definition and a more usual one is that all the solute species obey Henry's Law (466). From this starting-point Raoult's Law may be deduced directly by making use of the Duhem-Margules relation (387)

$$dT = 0 \quad dP = 0 \quad N_0 d \log p_0 + \sum_s N_s d \log p_s = 0. \quad (472)$$

But according to Henry's Law (466),

$$d \log p_s = d \log N_s, \quad (473.1)$$

and so

$$N_s d \log p_s = d N_s, \quad (473.2)$$

and

$$\begin{aligned} \sum_s N_s d \log p_s &= \sum_s d N_s \\ &= -d N_0. \end{aligned} \quad (473.3)$$

We therefore have

$$d \log p_0 = \frac{dN_0}{N_0} = d \log N_0. \quad (473.4)$$

Integration of (473.4) leads directly to Raoult's Law (471).

*Osmotic Pressure of Ideal Solution.*—Let us consider a solution  $\alpha$  at a pressure  $P^\alpha$  in osmotic equilibrium with the pure solvent  $\beta$  at a pressure  $P^\beta$ , both solution and pure solvent being at the same temperature  $T$ . Then the chemical potential  $\mu_0^\alpha$  of the solvent in the solution is, according to (462.3), given by

$$\mu_0^\alpha = \mu_0^*(T) + P^\alpha V_0^* \{1 - \frac{1}{2} \kappa_0 P^\alpha\} + RT \log N_0, \quad (474.1)$$

while  $\mu_0^\beta$  that of the pure solvent is similarly given by

$$\mu_0^\beta = \mu_0^*(T) + P^\beta V_0^* \{1 - \frac{1}{2} \kappa_0 P^\beta\}. \quad (474.2)$$

But the condition for osmotic equilibrium is, according to (90), simply

$$\mu_0^\alpha = \mu_0^\beta. \quad (474.3)$$

Substituting (474.1) and (474.2) into (474.3), we obtain

$$P^\alpha V_0^* \{1 - \frac{1}{2} \kappa_0 P^\alpha\} + RT \log N_0 = P^\beta V_0^* \{1 - \frac{1}{2} \kappa_0 P^\beta\}, \quad (474.4)$$

or

$$RT \log \frac{1}{N_0} = (P^\alpha - P^\beta) V_0^* \{1 - \frac{1}{2} \kappa_0 (P^\alpha + P^\beta)\}. \quad (474.5)$$

Let us use the symbol  $[V_0]$  to denote the partial molar volume of the solvent at the given temperature and at a pressure equal to the mean of  $P^\alpha$  and  $P^\beta$ . Then

$$[V_0] = V_0^* \{1 - \frac{1}{2} \kappa_0 (P^\alpha + P^\beta)\}. \quad (474.6)$$

Substituting (474.6) into (474.5), we obtain

$$RT \log \frac{1}{N_0} = (P^\alpha - P^\beta) [V_0]. \quad (474.7)$$

The osmotic pressure  $\Pi$  is therefore given by

$$\Pi = P^\alpha - P^\beta = \frac{RT}{[V_0]} \log \frac{1}{N_0}. \quad (475)$$

From (475) we see that the osmotic pressure  $\Pi$  depends on the external pressure  $P^\beta$  on the pure solvent only in so far as the value of  $[V_0]$  depends on  $P^\beta$ . If, as is usual,  $P^\beta$  is one atmosphere

or less, then  $\kappa_0 P^\beta$  will be negligibly small compared with unity, and (474.5) approximates to

$$RT \log \frac{1}{N_0} = (P^\alpha - P^\beta) V_0^* \{1 - \frac{1}{2} \kappa_0 (P^\alpha - P^\beta)\}, \quad (476.1)$$

and the osmotic pressure  $\Pi$  is then given by

$$\Pi \{1 - \frac{1}{2} \kappa_0 \Pi\} = \frac{RT}{V_0^*} \log \frac{1}{N_0}, \quad (476.2)$$

which does not involve  $P^\beta$  the pressure on the pure solvent.

If the osmotic pressure  $\Pi$  itself is sufficiently small for  $\kappa_0 \Pi$  to be negligible compared with unity, then (476.2) simplifies still further to

$$\Pi = \frac{RT}{V_0^*} \log \frac{1}{N_0}. \quad (476.3)$$

The approximate formula (476.2) for the osmotic pressure  $\Pi$  may alternatively be obtained by using formula (425), according to which  $\Pi$  is given by

$$\int_0^\Pi V_0 d\Pi = RT \log \frac{p_0^\circ}{p_0}, \quad (477)$$

where  $p_0^\circ$ ,  $p_0$  are respectively the vapour pressure of the pure solvent at a low (effectively zero) external pressure, and the partial vapour pressure of the solvent in the solution at the same low external pressure.  $V_0$  denotes the partial molar volume of the solvent in the solution when the external pressure is  $\Pi$ . But for an ideal solution, according to (459),  $V_0$  is independent of the composition of the solution and is given by

$$V_0 = V_0^* (1 - \kappa_0 \Pi), \quad (478)$$

where  $V_0^*$  is the molar volume of the solvent at zero pressure and  $\kappa_0$  is the compressibility of the solvent. We can therefore perform the integration in (477), and obtain

$$\Pi V_0^* \{1 - \frac{1}{2} \kappa_0 \Pi\} = RT \log \frac{p_0^\circ}{p_0}. \quad (479)$$

Finally, substituting the value of  $p_0$  given by Raoult's Law (471), we obtain

$$\Pi V_0^* \{1 - \frac{1}{2} \kappa_0 \Pi\} = RT \log \frac{1}{N_0}, \quad (480)$$

which is the same as (476.2).



*Freezing-point of Ideal Solution.*—In the shorthand notation introduced in the last chapter, we have for the variation of the chemical potential of the solvent species at constant temperature and pressure in an ideal solution according to (458)

$$D\mu_0 = RTd \log N_0. \quad (482)$$

Hence, formula (446) for the dependence of the freezing-point on the composition becomes

$$\frac{L_F}{T}dT = RTd \log N_0, \quad (483)$$

where  $L_F$  denotes the molar heat of fusion of the solvent at the freezing-point of the solution. As we are considering variations of the equilibrium between solution and pure solid solvent at a given *constant pressure*, we may use Kirchhoff's formula (179)

$$\frac{dL_0}{dT} = C^L - C^S, \quad (484)$$

where  $C^L$  and  $C^S$  are the molar heat capacities at constant pressure of the pure liquid and the pure solid solvent. Within the range of temperature between the freezing-point of the solution and that of the pure solvent, it will generally be permissible to regard the value of  $C^L - C^S$  as independent of the temperature. On this assumption (484) may be integrated to

$$L_F = L_F^\circ + (C^L - C^S)(T - T^\circ), \quad (485)$$

where  $L_F^\circ$  is the molar heat of fusion of the pure solvent at its freezing-point  $T^\circ$ . Substituting from (485) into (483), we obtain

$$d \log N_0 = \left\{ \frac{L_F^\circ}{RT^2} + \frac{(C^L - C^S)(T - T^\circ)}{RT^2} \right\} dT. \quad (486)$$

Integrating this we obtain

$$\begin{aligned} \log \frac{1}{N_0} &= \int_T^{T^\circ} \left\{ \frac{L_F^\circ}{RT^2} + \frac{(C^L - C^S)(T - T^\circ)}{RT^2} \right\} dT \\ &= \frac{L_F^\circ}{R} \left\{ \frac{1}{T} - \frac{1}{T^\circ} \right\} + \frac{(C^L - C^S)}{R} \left\{ \log \frac{T^\circ}{T} + 1 - \frac{T^\circ}{T} \right\}. \end{aligned} \quad (487)$$

Writing  $\theta$  for the lowering of freezing-point, given by

$$\theta = T^\circ - T, \quad (488)$$

expanding in powers of  $\frac{\theta}{T^0}$ , and neglecting the cube of this quantity (we are already neglecting terms of this order in assuming  $CL - CS$  to be independent of the temperature), we obtain

$$\begin{aligned}\log \frac{I}{N_0} &= \frac{L_F^0}{RT^{02}} \left\{ \theta + \frac{\theta^2}{T^0} \right\} + \frac{CL - CS}{RT^0} \left\{ \theta + \frac{1}{2} \frac{\theta^2}{T^0} - \theta - \frac{\theta^2}{T^{02}} \right\} \\ &= \frac{L_F^0}{RT^{02}} \cdot \theta + \frac{\theta^2}{T^{02}} \left\{ \frac{L_F^0}{RT^0} - \frac{1}{2} \frac{CL - CS}{R} \right\}.\end{aligned}\quad (489)$$

At high dilutions the term in  $\left(\frac{\theta}{T^0}\right)^2$  will be small, and we then have approximately

$$\log \frac{I}{N_0} = \frac{L_F^0}{RT^{02}} \theta, \quad (490)$$

a formula which, in a less exact form, is due to van't Hoff.

*Boiling-point of Ideal Solution.*—Provided all the solute species may be regarded as non-volatile, the boiling-point of a solution is the temperature at which it is in equilibrium as regards the solvent species with the vapour of the pure solvent at a given pressure (usually one atmosphere). The derivation of formulæ for the dependence of the boiling-point on the composition for ideal solutions is exactly analogous to that in the case of the freezing-point. The formula obtained is

$$\log \frac{I}{N_0} = \frac{L_E^0}{RT^{02}} \theta + \frac{\theta^2}{T^{02}} \left\{ -\frac{L_E^0}{RT^0} - \frac{1}{2} \frac{CL - C^G}{R} \right\}. \quad (491)$$

Here  $T^0$  is the boiling-point of the pure solvent,  $\theta$  is the rise of boiling-point of the solution above that of the pure solvent,  $L_E$  is the molar heat of evaporation of the solvent at the boiling-point of the pure solvent.  $CL$ ,  $C^G$  are the molar heat capacities at constant pressure of the solvent in the liquid and gaseous states respectively. Formula (491) is accurate provided terms of the order  $\left(\frac{\theta}{T^0}\right)^3$  are negligible. At high dilutions, when terms of the order  $\left(\frac{\theta}{T^0}\right)^2$  are negligible, (491) simplifies to

$$\log \frac{I}{N_0} = \frac{L_E^0}{RT^{02}} \theta, \quad (492)$$

a formula, which, in a less exact form, is due to van't Hoff.

*Solubility in Ideal Solutions.*—According to (458) the chemical

potential of each solute species at given temperature and pressure in an ideal solution is determined completely by its own mole fraction, and is independent of the mole fractions of all the other solute species. It follows that for all solutions of given temperature and pressure saturated with respect to the species  $s$  we have

$$N_s = \text{constant.} \quad (493)$$

This constant value of  $N_s$  is the "solubility" of  $s$  at the given temperature and pressure.

For the dependence of the solubility on the temperature we have, according to (443) and (458),

$$\frac{L_s}{T} dT = RT d \log N_s, \quad (494)$$

or

$$\frac{d \log N_s}{dT} = \frac{L_s}{RT^2}, \quad (495)$$

where  $L_s$  is the molar heat of solution of  $s$ , i.e. the heat *absorbed* when one mole of the pure solid  $s$  is dissolved.

*Nernst's Distribution Law.*—For the equilibrium as regards the solute species  $s$  between two solutions, both ideal but in different solvents, we have the condition (382)

$$p_s^\alpha = p_s^\beta, \quad (496)$$

where the indices  $\alpha$  and  $\beta$  refer to the two different solvents. As both solutions are by supposition ideal, Henry's Law (466) is obeyed in each, so that

$$p_s^\alpha = k^\alpha N_s^\alpha, \quad (497.1)$$

$$p_s^\beta = k^\beta N_s^\beta. \quad (497.2)$$

Substituting from (497) into (496), we obtain

$$\frac{N_s^\beta}{N_s^\alpha} = \frac{k_s^\alpha}{k_s^\beta} = l_s, \quad (498)$$

where  $l_s$  is for a given pair of solvents at given temperature and pressure constant.  $l_s$  is called the "partition coefficient" for the solute species  $s$  between the two solvents  $\alpha$  and  $\beta$ . Formula (498) is known as Nernst's Distribution Law for ideal solutions.

By comparing (467) and (498), we obtain for the dependence of  $l_s$  on the temperature

$$\begin{aligned} \frac{\partial \log l_s}{\partial T} &= \frac{\partial \log k_s^\alpha}{\partial T} - \frac{\partial \log k_s^\beta}{\partial T} \\ &= \frac{L_s^{\alpha \rightarrow \beta}}{RT^2}, \end{aligned} \quad (499)$$

where  $L_s^{\alpha \rightarrow \beta}$  is the heat absorbed when a mole of  $s$  is transferred from the solvent  $\alpha$  to the solvent  $\beta$ .

*Law of Mass Action for Ideal Solutions.*—If we substitute in the general law of mass action (384),

$$\frac{(p_Q)^q \cdot (p_R)^r}{(p_L)^l \cdot (p_M)^m} = K(T), \quad (500)$$

from Henry's Law (466), which in an ideal solution will hold for each species we obtain

$$\begin{aligned} \frac{(N_Q)^q \cdot (N_R)^r}{(N_L)^l \cdot (N_M)^m} &= K \frac{(k_L)^l \cdot (k_M)^m}{(k_Q)^q \cdot (k_R)^r} \\ &= K'(T, P), \end{aligned} \quad (501)$$

where  $K'$  is for a given solvent, temperature and pressure a constant.

For the dependence of  $K'$  on the temperature we obtain, by comparing (501), (348) and (467),

$$\frac{\partial \log K'}{\partial T} = \frac{L}{RT^2}. \quad (502)$$

$L$  is the heat of reaction at constant pressure in the given solvent. That is to say,  $L$  denotes the increase in the total heat content or the heat absorbed when the reaction takes place to the extent

$$lL + mM \rightarrow qQ + rR, \quad (503)$$

at constant temperature and pressure in the given solvent.

Similarly, for the dependence of  $K'$  on the pressure, we obtain, by comparing (501) and (468),

$$\frac{\partial \log K'}{\partial P} = -\frac{\Delta V}{RT}, \quad (504)$$

where  $\Delta V$  denotes the increase in volume when the reaction takes place to the extent

$$lL + mM \rightarrow qQ + rR, \quad (505)$$

at constant temperature and pressure in the given solvent.

## NOTES AND REFERENCES

*Laws of Ideal Solutions.*—The laws of ideal solution were given in their exact form by G. N. Lewis in *J. Am. Chem. Soc.*, **30**, 668 (1908), and by Washburn in *Z. Physik. Chem.*, **74**, 537 (1910). These authors' attempts to deduce them from molecular kinetic considerations are, however, open to criticism, *vide* Guggenheim, *J. Phys. Chem.*, **34**, 1751 (1930). Their derivation by statistical mechanical methods has been given recently by Guggenheim in *Proc. Roy. Soc.*, **135**, 181 (1932).

*Osmotic Pressure.*—The formula for the osmotic pressure of an ideal solution in the exact and yet compact form (475) was given by Donnan and Guggenheim, *Z. Physik. Chem.*, A, **162**, 346 (1932).

## CHAPTER VII

### SEMI-IDEAL SOLUTIONS

*(Solutions which mix at constant temperature and pressure without absorption or emission of heat and without volume contraction or expansion.)*

*Significance of "Semi-ideal" Solutions.*—We saw in the last chapter that amongst the properties of Ideal Solutions are the two following:—

1. Two ideal solutions in the same solvent mix at constant temperature and pressure without absorption or emission of heat. In other words, the partial molar heat content  $H_i$  of each species, whether solvent or solute, is independent of the composition.
2. Two ideal solutions in the same solvent mix at constant temperature and pressure without volume expansion or contraction. In other words, the partial molar volume  $V_i$  of each species, whether solvent or solute, is independent of the composition.

It is possible for certain solutions to have these two properties without having all the other properties of ideal solutions. As a matter of fact, most aqueous solutions of strong electrolytes at concentrations below tenth molar mix with only very slight heat effect or volume change. For want of a better name, solutions with these two properties may be called "semi-ideal" solutions. As the thermodynamic properties of these solutions are somewhat simpler than those of the more general "non-ideal solutions," it seems worth while devoting a chapter to them.

*Chemical Potentials and Activity Coefficients in Semi-ideal Solutions.*—Since solutions of any solute in any solvent tend to become ideal as the dilution becomes very great, we have for the chemical potential of any species  $i$ , whether solvent or solute

$$\mu_i = \mu_i^\circ(T, P) + RT \log N_i. \quad (506)$$

provided the dilution is sufficiently great. At less high dilutions where the solution is no longer ideal, we may write formally

$$\begin{aligned}\mu_i &= \mu_i^\circ(T, P) + RT \log N_i + RT \log f_i \\ &= \mu_i^\circ(T, P) + RT \log N_i f_i.\end{aligned}\quad (507)$$

$f_i$  will in general be a function of the temperature, pressure and composition of the solution, and is called the "activity coefficient" of the species  $i$ . The conception and name of this useful function are due to G. N. Lewis. All we know about  $f_i$  in general is that at a given temperature and pressure  $f_i$  tends to unity at infinite dilution, that is to say,

$$f_i \rightarrow 1 \text{ and } f_s \rightarrow 1 \quad \text{as } N_i \rightarrow 1 \text{ and } N_s \rightarrow 0. \quad (508)$$

At finite concentrations when the solution is no longer ideal,  $1 - f_i$ , or alternatively  $\log f_i$ , is a convenient measure of the deviation of the solution from ideality so far as the species  $i$  is concerned.

According to (173) we have

$$\frac{\partial \mu_i / T}{\partial T} = - \frac{H_i}{T^2}. \quad (509)$$

Applying this to the actual solution and to an infinitely dilute solution in the same solvent at the same temperature and pressure, and subtracting we obtain

$$\frac{\partial \log f_i}{\partial T} = - \frac{H_i - H_i^\circ}{RT^2}. \quad (510)$$

where  $H_i^\circ$  is the value of  $H_i$  at infinite dilution. But by the definition of a "semi-ideal" solution

$$H_i = H_i^\circ, \quad (511)$$

and so

$$\frac{\partial \log f_i}{\partial T} = 0. \quad (512)$$

Similarly, according to (153) we have

$$\frac{\partial \mu_i}{\partial P} = v_i. \quad (513)$$

Applying this to the actual solution and to an infinitely dilute solution in the same solvent at the same temperature and pressure, and subtracting, we obtain

$$\frac{\partial \log f_i}{\partial P} = \frac{V_i - V_i^\circ}{RT}, \quad (514)$$

where  $V_i^\circ$  is the value of  $V_i$  at infinite dilution. But by the definition of a "semi-ideal" solution

$$V_i = V_i^\circ, \quad (515)$$

and so

$$\frac{\partial \log f_i}{\partial P} = 0. \quad (516)$$

According to (512) and (516), we see that semi-ideal solutions have the important property that the activity coefficient  $f_i$  of each species, whether solvent or solute, is a function of the composition (expressed in terms of the mole fraction of the various species) independent of temperature and pressure.

*Alternative Form for Chemical Potential.*—Owing to the fact that the partial molar volume of each species in a semi-ideal solution is independent of the composition, we may just as for an ideal solution write

$$V_i = V_i^*(1 - \kappa_i P), \quad (517.1)$$

where  $V_i^*$  the partial molar volume at zero pressure and the compressibility coefficient  $\kappa_i$  are independent both of the pressure and of the composition. The values of  $V_i^*$  and  $\kappa_i$  will depend on the temperature as well as the solvent. It follows from (153), (507) and (517.1) that  $\mu_i$  must be of the form

$$\mu_i = \mu_i^*(T) + PV_i^*(1 - \frac{1}{2}\kappa_i P) + RT \log N_i f_i, \quad (517.2)$$

where  $\mu_i^*$ ,  $V_i^*$ ,  $\kappa_i$  are determined entirely by the temperature and the solvent, while  $f_i$  is in a given solvent a function of the composition only.

*Relation between Activity Coefficients.*—If we substitute from (507) in the Gibbs-Duhem relation (33), we have, using the operator  $D$  to refer to variations of composition at constant temperature and pressure,

$$\sum_i N_i D \log N_i + \sum_i N_i D \log f_i = 0. \quad (518.1)$$

But the sum on the left vanishes identically, and so (518.1) reduces to

$$\sum_i N_i D \log f_i = 0. \quad (518.2)$$

But as the activity coefficients in semi-ideal solutions, regarded as functions of the composition expressed in mole



fractions, are independent of the temperature and pressure, we may omit in (518.2) the restrictions of constancy of temperature and pressure. We thus obtain for a variation of composition, even if accompanied by variation of temperature and pressure,

$$\sum_i N_i d \log f_i = 0, \quad (519.1)$$

or distinguishing between solvent species and solute species

$$N_0 d \log f_0 + \sum_s N_s d \log f_s = 0 \quad (519.2)$$

If therefore we know how the activity coefficient  $f_s$  of each solute species depends on the composition, we can deduce how the activity coefficient  $f_0$  of the solvent depends on the composition.

Alternatively, if we know the dependence on the composition of the activity coefficients of the solvent and of all the solute species except one, we can calculate that of the activity coefficient of the remaining solute species. In particular, for a solution containing only one solute species, if we know the dependence on the composition of the activity coefficient of the solvent we can calculate that of the activity coefficient of the solute.

*Osmotic Coefficient of Solvent.*—Amongst the most important examples of semi-ideal solutions are aqueous solutions of univalent strong electrolytes at dilutions where the mole fractions  $N_s$  of the solute species are of the order of magnitude  $10^{-6}$  to  $10^{-3}$ . For such solutions the activity coefficients  $f_s$  of the solute species differ from unity by anything from 1 per cent. to 15 per cent. Clearly these solutions are by no means ideal. Nevertheless, if one uses the relation (519) to compute the activity coefficient of the water  $f_0$ , one finds that it differs from unity by only one part in  $10^9$  to one part in  $10^4$ . Thus, for purely numerical reasons the activity coefficient  $f_0$  of the solvent species, in contrast to the activity coefficient  $f_s$  of the solute species, is not always a convenient function for measuring deviations from ideality. It is therefore useful to introduce another function  $g$  called the "osmotic coefficient" of the solvent defined by the relation

$$\mu_0 = \mu_0^\circ + gRT \log N_0 \quad (520.1)$$

where

$$g \rightarrow 1 \quad \text{as } N_0 \rightarrow 1 \quad \text{and } N_s \rightarrow 0. \quad (520.2)$$

The conception and name of this useful function are due to Bjerrum.

It is easy to show that for a semi-ideal solution the osmotic coefficient  $g$  is a function of the composition (expressed in

terms of the mole fractions of the components) independent of temperature and pressure. The proof is exactly analogous to that for the same property of the activity coefficients.

Comparison of (520) with (517.2) shows that we may express the chemical potential  $\mu_0$  of the solvent species in the form

$$\mu_0 = \mu_0^*(T) + PV_0^*\{1 - \frac{1}{2}\kappa_0 P\} + gRT \log N_0, \quad (521)$$

where  $\mu_0^*$  the chemical potential of the pure solvent at zero pressure,  $V_0^*$  the molar volume of the pure solvent at zero pressure and  $\kappa_0$  the compressibility of the pure solvent depend only on the temperature, while the osmotic coefficient  $g$  is a function only of the composition of the solution.

*Relation between Osmotic Coefficient and Activity Coefficients.*

—Comparison of the definition of the activity coefficient  $f_0$  of the solvent (507)

$$\mu_0 = \mu_0^\circ + RT \log N_0 + RT \log f_0, \quad (522)$$

and the definition of the osmotic coefficient (520)

$$\mu_0 = \mu_0^\circ + gRT \log N_0, \quad (523)$$

shows that these two functions are related by

$$\log f_0 = (1 - g) \log \frac{1}{N_0}. \quad (524)$$

Substituting (524) into (519.2), we obtain as the relation between variations of the osmotic coefficient of the solvent species and the activity coefficients of the solute species

$$N_0 d\left\{(1 - g) \log \frac{1}{N_0}\right\} + \sum_s N_s d \log f_s = 0, \quad (525)$$

or

$$-N_0 \log \frac{1}{N_0} \cdot dg - (1 - g)dN_0 + \sum_s N_s d \log f_s = 0, \quad (526)$$

or

$$-N_0 \log \frac{1}{N_0} \cdot dg + (1 - g)\sum_s dN_s + \sum_s N_s d \log f_s = 0. \quad (527)$$

These formulæ, like (519.2), hold for variations of composition of a semi-ideal solution, whether or not the temperature and pressure are also varied.

For aqueous solutions of strong electrolytes the osmotic coefficient differs from unity by fractional amounts of the same order of magnitude as do the activity coefficients of the solute

species. It is therefore numerically a more convenient function than the activity coefficient of the solvent.

*Usefulness of Activity Coefficients and Osmotic Coefficient.*—The usefulness of the activity coefficients is that all the equilibrium properties of each solute species can be expressed in terms of the activity coefficient of this species. Similarly, all the equilibrium properties of the solvent can be expressed in terms of either its activity coefficient or its osmotic coefficient, the two being related by (524). Each of these coefficients becomes unity in the special case of ideal solutions. Thus, the formulæ for ideal solutions are obtained from those for ordinary dilute solutions by replacing all the  $f_i$  and  $g$  throughout by unity. When these coefficients have not the value unity, the deviations from unity are a convenient measure of the deviations from ideality. Thermodynamics can, of course, neither predict nor explain the magnitude of such deviations. Any such explanation must be of a non-thermodynamic nature, based on kinetic theory.

The deduction of the formulæ for the various properties of semi-ideal solutions proceeds on exactly the same lines as in the case of ideal solutions. Only formulæ (507), (517.2), (520), (521), have to be used in place of (458), (462.3). It is therefore scarcely necessary to do more than give the formulæ thus obtained.

*Vapour Pressure of Solute.*—Instead of Henry's Law for ideal solutions, we obtain for semi-ideal solutions for the vapour pressure of the solute species

$$p_s = k_s N_s f_s, \quad (528)$$

where  $f_s$  is a function of the composition (expressed in terms of the mole fractions  $N_i$ ) independent of temperature and pressure, while  $k_s$  is a function of temperature and pressure independent of the concentration. At high dilutions  $f_s$  tends to unity. The dependence of  $k_s$  on temperature and pressure is given by (467) and (468).

*Vapour Pressure of Solvent.*—Instead of Raoult's Law for the vapour pressure of the solvent in an ideal solution, we obtain in a semi-ideal solution the alternative formulæ

$$p_0 = p_0^\circ N_0 f_0, \quad (529.1)$$

$$p_0 = p_0^\circ (N_0)^g \quad (529.2)$$

where  $p_0^\circ$  is the vapour pressure of the pure solvent at the given temperature and pressure.

*Osmotic Pressure of Semi-Ideal Solution.*—To obtain the formula for the osmotic pressure of a semi-ideal solution we

proceed in exactly the same manner as we did for an ideal solution. We consider a solution  $\alpha$  at a pressure  $P^\alpha$  in osmotic equilibrium with the pure solvent  $\beta$  at a pressure  $P^\beta$ , both solution and pure solvent being at the same temperature  $T$ . Then the chemical potential  $\mu_0^\alpha$  of the solvent in the solution is, according to (517.2), given by

$$\mu_0^\alpha = \mu_0^*(T) + P^\alpha V_0^* \left\{ 1 - \frac{1}{2} \kappa_0 P^\alpha \right\} + gRT \log N_0, \quad (530.1)$$

while  $\mu_0^\beta$  that of the pure solvent is similarly given by

$$\mu_0^\beta = \mu_0^*(T) + P^\beta V_0^* \left\{ 1 - \frac{1}{2} \kappa_0 P^\beta \right\}. \quad (530.2)$$

But the condition for osmotic equilibrium is simply

$$\mu_0^\alpha = \mu_0^\beta. \quad (530.3)$$

Substituting (530.1) and (530.2) into (530.3), we obtain

$$P^\alpha V_0^* \left\{ 1 - \frac{1}{2} \kappa_0 P^\alpha \right\} + gRT \log N_0 = P^\beta V_0^* \left\{ 1 - \frac{1}{2} \kappa_0 P^\beta \right\}, \quad (530.4)$$

or

$$gRT \log \frac{1}{N_0} = (P^\alpha - P^\beta) V_0^* \left\{ 1 - \frac{1}{2} \kappa_0 (P^\alpha + P^\beta) \right\}. \quad (530.5)$$

Just as in the case of ideal solutions, let us introduce the symbol  $[V_0]$  to denote the partial molar volume of the solvent at the given temperature and at a pressure equal to the mean of  $P^\alpha$  and  $P^\beta$ . Then

$$[V_0] = V_0^* \left\{ 1 - \kappa_0 \frac{P^\alpha + P^\beta}{2} \right\}. \quad (530.6)$$

Substituting (530.6) into (530.5), we obtain

$$gRT \log \frac{1}{N_0} = (P^\alpha - P^\beta) [V_0]. \quad (530.7)$$

The osmotic pressure  $\Pi$  is therefore given by

$$\Pi = P^\alpha - P^\beta = g \frac{RT}{[V_0]} \log \frac{1}{N_0}. \quad (531)$$

From (531) we see that the osmotic pressure  $\Pi$  depends on the external pressure  $P^\beta$  on the pure solvent only in so far as the value of  $[V_0]$  depends on  $P^\beta$ . If, as is usual,  $P^\beta$  is one atmosphere or less, then  $\kappa_0 P^\beta$  will be negligibly small compared with unity, and (530.5) approximates to

$$gRT \log \frac{1}{N_0} = (P^\alpha - P^\beta) V_0^* \left\{ 1 - \frac{1}{2} \kappa_0 (P^\alpha - P^\beta) \right\}, \quad (532.1)$$

and the osmotic pressure  $\Pi$  is then given by

$$\Pi\{1 - \frac{1}{2}\kappa_0\Pi\} = g\frac{RT}{V_0^*} \log \frac{1}{N_0}, \quad (532.2)$$

which does not involve  $P^B$  the pressure on the pure solvent.

If the osmotic pressure  $\Pi$  itself is sufficiently small for  $\kappa_0\Pi$  to be negligible compared with unity, then (532.2) simplifies still further to

$$\Pi = g\frac{RT}{V_0^*} \log \frac{1}{N_0}. \quad (532.3)$$

If we compare the exact formula (531) with the corresponding exact formula (475) for an ideal solution, or the approximate formula (532.3) with the corresponding approximate formula (476.3) for an ideal solution, in either case we find the osmotic pressure of the semi-ideal solution differs from the osmotic pressure of the ideal solution only by the factor  $g$ . That is to say, that the ratio of the actual osmotic pressure of a semi-ideal solution to its ideal value is equal to the osmotic coefficient  $g$ . This gives the explanation of the name "osmotic coefficient."

Formulae (531) and (532.3) may be written, in terms of the activity coefficient  $f_0$  of the solvent, in the alternative forms

$$\Pi = \frac{RT}{[V_0]} \log \frac{1}{N_0 f_0}, \quad (533.1)$$

and

$$\Pi = \frac{RT}{V_0^*} \log \frac{1}{N_0 f_0}. \quad (533.2)$$

*Freezing-point.*—In the shorthand notation of Chapter V, we have for a semi-ideal solution

$$D\mu_0 = d(gRT \log N_0), \quad (534)$$

and so

$$\int_{N_0}^{N_1} D\mu_0 = gRT \log N_0. \quad (535)$$

It follows that for the lowering of freezing-point  $\theta$  we obtain, in place of (489) holding for ideal solutions,

$$g \log \frac{1}{N_0} = \frac{I_F^\circ}{RT^{\circ 2}} \theta + \frac{\theta^2}{T^{\circ 2}} \left\{ \frac{L_F^\circ}{RT^\circ} - \frac{1}{2} \frac{C^L - C^S}{R} \right\}, \quad (536)$$

where  $T^\circ$  is the freezing-point of the pure solvent,  $L_F^\circ$  its molar heat of fusion at its freezing-point,  $C^L$  and  $C^S$  the molar heat

capacities at constant pressure in the liquid and solid state. Formula (536) is accurate, neglecting terms in  $\left(\frac{\theta}{T^\circ}\right)^3$ .

At high dilutions the term in  $\left(\frac{\theta}{T^\circ}\right)^2$  will be small, and we then have approximately

$$g \log \frac{1}{N_0} = \frac{L_F^\circ}{RT^{\circ 2}} \theta. \quad (537)$$

*Boiling-point.*—For the rise  $\theta$  of boiling-point over that of the pure solvent  $T^\circ$  we obtain, in an exactly similar manner,

$$g \log \frac{1}{N_0} = \frac{L_E^\circ}{RT^{\circ 2}} \theta + \frac{\theta^2}{T^{\circ 2}} \left\{ -\frac{L_E^\circ}{RT^\circ} - \frac{1}{2} \frac{C^L - C^G}{R} \right\}, \quad (538)$$

where  $L_E^\circ$  is the molar heat of evaporation of the solvent (at constant pressure) at its boiling-point  $T^\circ$ ,  $C^L$  and  $C^G$  are the molar heat capacities at constant pressure of the solvent in the liquid and vapour states respectively. Formula (538) is accurate, neglecting terms in  $\left(\frac{\theta}{T^\circ}\right)^3$ .

If the solution is sufficiently dilute the term in  $\left(\frac{\theta}{T^\circ}\right)^2$  will be negligible, in which case (538) simplifies to

$$g \log \frac{1}{N_0} = \frac{L_E^\circ}{RT^{\circ 2}} \theta. \quad (539)$$

*Solubility.*—The solubility  $N_s$  of the solid phase of pure  $s$  in an ordinary dilute solution may depend on the concentration of other solute species present in the solution. All solutions of various compositions, in a given solvent at given temperature and pressure, saturated with respect to the solid phase of pure  $s$ , are related by

$$N_s f_s = \text{constant}. \quad (540)$$

In other words, in solutions of various compositions saturated with respect to the solid phase of pure  $s$ , the activity coefficient of  $s$  is inversely proportional to its solubility expressed as mole fraction.

The dependence of solubility on the temperature is still given by (495).

*Distribution between Two Solvents.*—For the equilibrium as

regards the solute species  $s$  between two solvents  $\alpha$  and  $\beta$ , we have the condition

$$\frac{[N_s f_s]^\beta}{[N_s f_s]^\alpha} = l_s, \quad (541)$$

or

$$\frac{N_s^\beta}{N_s^\alpha} = l_s \frac{f_s^\alpha}{f_s^\beta}. \quad (542)$$

Thus the ratio of the mole fraction of  $s$  in the two phases is inversely proportional to its activity coefficient in the two phases.

The partition coefficient  $l_s$  depends on the temperature according to (499).

In the special case that the solutions of  $s$  in the solvent  $\beta$ , but not in the solvent  $\alpha$ , are ideal (542) becomes

$$\frac{N_s^\beta}{N_s^\alpha} = l_s f_s^\alpha. \quad (543)$$

*Law of Mass Action.*—The law of mass action for semi-ideal solutions takes the form

$$\frac{(N_Q f_Q)^q \cdot (N_R f_R)^r}{(N_L f_L)^l \cdot (N_M f_M)^m} = K' (T, P), \quad (544)$$

where the equilibrium constant  $K'$  is for given solvent, temperature and pressure a constant. The dependence of  $K'$  on the temperature and pressure is given by (502) and (504).

Alternatively (544) may be written

$$\frac{(N_Q)^q \cdot (N_R)^r}{(N_L)^l \cdot (N_M)^m} = K' \frac{(f_L)^l \cdot (f_M)^m}{(f_Q)^q \cdot (f_R)^r}. \quad (545)$$

The two sides of this equation are not constant, but depend on the composition according to the dependence of the activity coefficients on the composition. It is therefore misleading to call these expressions "equilibrium constants". A more suitable name is the "equilibrium mole fractions product".

*Determination of Activity Coefficients and Osmotic Coefficient.*—According to formulæ (529), (536), (538), (531), it is clear that the activity coefficient  $f_o$  of the solvent or the osmotic coefficient  $g$  in a given solution can be calculated directly from either a comparison of the vapour pressure of the solvent in the solution and in the pure state, or from a comparison of the freezing-points of the solution and of the pure solvent, or from a comparison of the boiling-points of the solution and of the pure

solvent, or from a measurement of the osmotic pressure. Any one of these determinations is effectively a measurement of the difference in the chemical potentials of the solvent in the given solution and in the pure solvent. A comparison of this measured value of difference in the chemical potential with the corresponding value for an ideal solution gives immediately the value of the activity coefficient of the solvent or the osmotic coefficient.

To obtain information concerning the activity coefficient  $f_s$  of a solute species, whether by measurement of vapour pressure, or by measurement of partition with another solvent, or by measurement of solubility (or as we shall see in Chapter X, by electrometric measurements), one has to make measurements on at least two solutions. Then, according to one of the formulæ (528), (543), (540), such a pair of measurements will determine the ratio of the values of the activity coefficient  $f_s$  in the two solutions. The absolute value of the activity coefficient in the one solution is determinable only if the other solution is so dilute as to be ideal, in which case all activity coefficients in it are unity. When accurate measurements are not possible in solutions so dilute as to be ideal, it is impossible to determine with certainty the absolute values of the activity coefficients. If, however, from kinetic molecular considerations one can predict the form of the dependence of the activity coefficient on the concentrations at high dilutions (for example, that  $\log f_s$  is proportional to some particular power of the concentration of solute), then extrapolation of the actual experimental measurements will serve in place of measurements at dilutions so high that the solutions are ideal.

In the case of only one solute species  $f_s$  the relations (519) and (527) between the activity coefficient  $f_s$  of the solute and the activity coefficient  $f_0$  or the osmotic coefficient  $g$  of the solvent become

$$(1 - N_s)d \log f_0 + N_s d \log f_s = 0, \quad (546)$$

$$- (1 - N_s) \log \frac{1}{1 - N_s} dg + (1 - g)dN_s + N_s d \log f_s = 0. \quad (547)$$

These may be written in the integrated forms

$$\log f_s = - \int_{N_s=0}^{N_s} \frac{1 - N_s}{N_s} d \log f_0, \quad (548)$$

$$\log f_s = \int_{N_s=0}^{N_s} \frac{1 - N_s}{N_s} \log \frac{1}{1 - N_s} dg - \int_{N_s=0}^{N_s} (1 - g) d \log N_s. \quad (549)$$



Thus the activity coefficient  $f_s$  of the solute species in a given semi-ideal solution can be computed if the activity coefficient  $f_0$  or osmotic coefficient  $g$  of the solvent is known not only for the given solution but for all solutions more dilute than the given solution. A knowledge of the values of  $f_0$  or  $g$  throughout the range of concentrations  $N'_s$  to  $N''_s$  makes possible the computation of the ratio of the values of  $f_s$  at the two concentrations  $N'_s$  and  $N''_s$ , but not their absolute values. Only if one of the concentrations, say  $N''_s$ , is so small that the solution is ideal, is the absolute value of  $f_s$  in the solution of concentration  $N'_s$  calculable.

#### NOTES AND REFERENCES.

See end of Chapter VIII.

*Distinction between Semi-ideal and Non-ideal Solutions.*—In Lewis and Randall's "Thermodynamics" a separate discussion of freezing-point is given for the two cases: (1) heat of dilution negligible; and (2) heat of dilution not negligible. This distinction corresponds to our division of solutions into the classes (1) semi-ideal; and (2) non-ideal.

## CHAPTER VIII

### NON-IDEAL SOLUTIONS

*Chemical Potentials and Activity Coefficients in Non-Ideal Solutions.*—We now pass on to the thermodynamic properties of the most general type of solution, that is one without any of the special characteristics of ideal solutions. We no longer assume that two solutions mix at constant temperature and pressure without any heat effect or without any volume change. Since solutions of any solute in any solvent tend to become ideal as the dilution becomes very great, we still write formally for the chemical potential of any species  $i$ , whether solvent or solute,

$$\mu_i = \mu_i^\circ(T, P) + RT \log N_i + RT \log f_i, \quad (550)$$

where  $\mu_i^\circ(T, P)$  is for a given solvent a function of the temperature and pressure only.  $f_i$ , called the activity coefficient of the species  $i$ , has the property that at given temperature and pressure  $f_i$  tends to unity at infinite dilution. That is to say:

$$f_0 \rightarrow 1 \text{ and } f_s \rightarrow 1 \quad \text{as } N_0 \rightarrow 1 \text{ and } N_s \rightarrow 0. \quad (551)$$

At finite concentrations when the solution is no longer ideal,  $1 - f_i$  or alternatively  $\log f_i$  are measures of the deviation of the solution from ideality so far as the species  $i$  is concerned.

All this is formally the same as for the "semi-ideal" solutions, discussed in Chapter VII, which mix at constant temperature and pressure without heat effect and without volume change. From these properties we deduced that the activity coefficients in semi-ideal solutions were functions of the composition (expressed in mole fractions) independent of temperature and pressure. This is, however, not the case for the activity coefficients of the general "non-ideal" solution.

By the same reasoning that led to (510), we obtain

$$\frac{\partial \log f_i}{\partial T} = - \frac{H_i - H_i^\circ}{RT^2}. \quad (552.1)$$

The physical meaning of the quantity  $H_i - H_i^\circ$  is the heat absorbed when one mole of the species  $i$  is transferred at constant

temperature and pressure to a large quantity of the actual solution from a large quantity of an infinitely dilute solution in the same solvent.  $H_i - H_i^\circ$  may be called the "heat of transference" of the species  $i$  from infinite dilution to the given solution.

Similarly, by the reasoning leading to (514), we obtain

$$\frac{\partial \log f_i}{\partial P} = \frac{V_i - V_i^\circ}{RT}. \quad (552.2)$$

The physical meaning of the quantity  $V_i - V_i^\circ$  is the expansion of volume when one mole of the species  $i$  is transferred at constant temperature and pressure to the actual solution from an infinitely dilute solution in the same solvent.

*Alternative Forms for Chemical Potentials.*—It is obvious that in the formula (550) for  $\mu_i$  the first term, which is independent of the composition, will at all concentrations have the same value as it does at infinite dilution at the same temperature and pressure. But at infinite dilution we may assume that all solutions become ideal. It follows that  $\mu_i^\circ(T, P)$  is of the form

$$\mu_i^\circ(T, P) = \mu_i^*(T) + PV_i^*(1 - \frac{1}{2}\kappa_i P), \quad (553.1)$$

where  $V_i^*$  is the value of  $V_i$  at zero pressure, and  $V_i^*(1 - \kappa_i P)$  is the value of  $V_i$  at the given pressure, in either case *not in the actual solution but in an infinitely dilute solution in the same solvent* at the given temperature.

Since  $\mu_i^*(T)$  is the value of  $\mu_i^\circ(T, P)$  at zero pressure, it follows that

$$\frac{d\mu_i^*/T}{dT} = -\frac{H_i^*}{T^2}, \quad (553.2)$$

where  $H_i^*$  is the value of  $H_i^\circ$  at zero pressure, that is the value of the partial molar heat content at infinite dilution at the given temperature and at zero pressure.

In particular for the solvent species we may write

$$\mu_0 = \mu_0^*(T) + PV_0^*(1 - \frac{1}{2}\kappa_0 P) + RT \log N_0 f_0, \quad (553.3)$$

where  $V_0^*$  and  $\kappa_0$  are respectively the molar volume at zero pressure and the compressibility of the *pure solvent* at the given temperature.

*Osmotic Coefficient of Solvent.*—Just as in the case of "semi-ideal" solutions the activity coefficient of the solvent, as opposed to those of the solute species, is for numerical reasons not the most suitable function for measuring deviations from ideality.

A more convenient function is the osmotic coefficient  $g$  defined by

$$\begin{aligned}\mu_0 &= \mu_0^\circ(T, P) + gRT \log N_0, \\ &= \mu_0^*(T) + PV_0^*(1 - \frac{1}{2}\kappa_0 P) + gRT \log N_0\end{aligned}\quad (554)$$

where

$$g \rightarrow 1 \text{ as } N_0 \rightarrow 1 \text{ and } N_s \rightarrow 0. \quad (555)$$

The osmotic coefficient  $g$  is accordingly related to the activity coefficient  $f_0$  of the solvent by

$$\log f_0 = (1 - g) \log \frac{1}{N_0}. \quad (556)$$

It follows from (556) and (552.1) that the dependence of the osmotic coefficient on the temperature is

$$\log \frac{1}{N_0} \cdot \frac{\partial g}{\partial T} = \frac{H_0 - H_0^\circ}{RT^2}. \quad (557)$$

Similarly, from (556) and (552.2) we deduce for the dependence of the osmotic coefficient on the pressure

$$\log \frac{1}{N_0} \cdot \frac{\partial g}{\partial P} = - \frac{V_0 - V_0^\circ}{RT}. \quad (558)$$

*Difference between Semi-Ideal Solutions and Non-Ideal Solutions.*—From the above considerations it follows that at given temperature and pressure the thermodynamic properties of the most general non-ideal solutions expressed in terms of activity coefficients or osmotic coefficients take the same form as for the more special semi-ideal solutions. It is only in the dependence of these activity coefficients and osmotic coefficients on the temperature and pressure according to (552.1), (552.2), (557), (558), that the differences appear. Most of the formulæ of Chapter VI therefore hold good for the more general type of non-ideal solution, provided that one assigns to the functions  $f_i$  and  $g$  their values at the appropriate temperature and pressure.

*Relation between Activity Coefficients and Osmotic Coefficient.*—As long as we restrict ourselves to variations at constant temperature and pressure, the relations between the activity coefficients take exactly the same form for non-ideal as for semi-ideal solutions. Thus, corresponding to (519.2), we have, using the symbol  $D$  to refer to variations of composition at constant temperature and pressure,

$$N_0 D \log f_0 + \sum_s N_s D \log f_s = 0. \quad (559.1)$$

In terms of the osmotic coefficient  $g$  we have, corresponding to (527), for changes of composition at constant temperature and pressure

$$-N_0 \log \frac{1}{N_0} Dg + (1-g) \sum_s dN_s + \sum_s N_s D \log f_s = 0, \quad (559.2)$$

a relation due to Bjerrum.

In particular for a solution containing only one solute species  $s$  (559.1) and (559.2), simplify to

$$(1 - N_s) D \log f_0 + N_s D \log f_s = 0, \quad (560.1)$$

$$- (1 - N_s) \log \frac{1}{1 - N_s} Dg + (1 - g) dN_s + N_s D \log f_s = 0. \quad (560.2)$$

These may be written in the integrated forms

$$\log f_s = - \int_{N_s=0}^{N_s} \frac{1 - N_s}{N_s} D \log f_0, \quad (560.3)$$

$$\log f_s = \int_{N_s=0}^{N_s} \frac{1 - N_s}{N_s} \log \frac{1}{1 - N_s} Dg - \int_{N_s=0}^{N_s} (1 - g) D \log N_s. \quad (560.4)$$

Thus the activity coefficient  $f_s$  of the solute species can, in a given non-ideal solution containing only the one solute, be computed if the activity coefficient  $f_0$  or the osmotic coefficient  $g$  of the solvent is known not only for the given solution but for all solutions more dilute than the given solution *at the same temperature and pressure*. Formula (560.3) is due to G. N. Lewis.

*Differential and Integral Heats of Dilution.*—If to a large (effectively infinite) quantity of a solution there be added at constant temperature and pressure one mole of pure solvent, the heat absorbed is called the “differential heat of dilution”. It is clearly identical with the molar heat of transference of the solvent species from the pure solvent to the actual solution, and is therefore equal to  $H_0 - H_0^\circ$ , where  $H_0$  is the partial molar heat content of the solvent species in the actual solution, and  $H_0^\circ$  the molar heat content of the pure solvent at the same temperature and pressure. It follows that the differential heat of dilution of a semi-ideal solution is zero.

If, on the other hand, to a finite quantity of a solution there be added at constant temperature and pressure sufficient solvent to dilute the solution until it becomes ideal, the heat absorbed is called the “integral heat of dilution.” For a quantity of

solution containing altogether one mole, it is clearly equal to the sum of the products of the mole fraction of each species, whether solvent or solute, with its partial molar heat of transference from the actual solution to an infinitely dilute solution (effectively pure solvent) at the same temperature and pressure. That is to say, its value  $L_D$  is given by

$$L_D = N_0(H_0^\circ - H_0) + \sum_s N_s(H_s^\circ - H_s), \quad (561)$$

where  $H_0$ ,  $H_s$  are the partial molar heat contents of solvent and solute species in the actual solution, and  $H_0^\circ$ ,  $H_s^\circ$  their values in an infinitely dilute solution at the same temperature and pressure. It follows from (561) that the integral heat of dilution of any semi-ideal solution is zero.

*Vapour Pressure of Solute.*—In exact analogy with (528) we have for non-ideal solutions

$$p_s = k_s N_s f_s, \quad (562)$$

where  $k_s$  is independent of  $N_s$  and  $f_s$  tends to unity at infinite dilution. The dependence of  $k_s$  on the temperature is according to (467)

$$\frac{\partial \log k_s}{\partial T} = \frac{L_s^\circ}{RT^2}, \quad (563)$$

where  $L_s^\circ$  denotes the molar heat of evaporation of  $s$  from an infinitely dilute solution. Combining this with (552.1) we obtain

$$\frac{\partial \log p_s}{\partial T} = \frac{L_s}{RT^2}, \quad (564)$$

where  $L_s$  is the molar heat of evaporation of  $s$  from the actual solution.

Similarly, the dependence of  $k_s$  on the external pressure is, according to (468),

$$\frac{\partial \log k_s}{\partial P} = \frac{V_s^\circ}{RT}, \quad (565)$$

where  $V_s^\circ$  is the partial molar volume of  $s$  in an infinitely dilute solution. Combining this with (552.2) we obtain, in agreement with (401),

$$\frac{\partial \log p_s}{\partial P} = \frac{V_s}{RT}, \quad (566)$$

where  $V_s$  is the partial molar volume of  $s$  in the actual solution.

*Vapour Pressure of Solvent.*—The formulæ for the vapour pressure of the solvent are exactly similar to those for a solute species, the coefficient  $k_0$  being equal to  $p_0^\circ$ , the vapour pressure

of the pure solvent at the given temperature and pressure. The relations are

$$p_0 = p_0^\circ N_0 f_0 = p_0^\circ (N_0)^g. \quad (567)$$

$$\frac{\partial \log p_0^\circ}{\partial T} = \frac{L_0^\circ}{RT^2}. \quad (568)$$

$$\frac{\partial \log p_0}{\partial T} = \frac{L_0}{RT^2}. \quad (569)$$

$$\frac{\partial \log p_0^\circ}{\partial P} = \frac{V_0^\circ}{RT}. \quad (570)$$

$$\frac{\partial \log p_0}{\partial P} = \frac{V_0}{RT}. \quad (571)$$

Here  $L_0$ ,  $L_0^\circ$  are the molar heats of evaporation of the solvent from the actual solution and from the pure solvent.

*Osmotic Pressure of Non-ideal Solution.*—To obtain the formula for the osmotic pressure of a non-ideal solution we proceed in exactly the same manner as we did in the cases of ideal and of semi-ideal solutions. We consider a solution  $\alpha$  at a pressure  $P^\alpha$  in osmotic equilibrium with the pure solvent  $\beta$  at a pressure  $P^\beta$ , both solution and pure solvent being at the same temperature  $T$ . By equating the values of the chemical potentials  $\mu_0^\alpha$  and  $\mu_0^\beta$  of the solvent in the two phases, we obtain, exactly as for a semi-ideal solution, for the osmotic pressure  $\Pi$  the formula

$$\Pi = P^\alpha - P^\beta = g \frac{RT}{[V_0]} \log \frac{1}{N_0}, \quad (572)$$

where  $[V_0]$  is the partial molar volume of the solvent at a pressure equal to the mean of  $P^\alpha$  and  $P^\beta$ , while  $g$  is the osmotic coefficient of the solvent in the solution at osmotic equilibrium, that is to say, at a pressure  $P^\alpha$ . The only distinction between the formula for a non-ideal and for a semi-ideal solution is that in the former case we must specify that  $g$  is to be given its value corresponding to the pressure  $P^\alpha$ , while in the latter case its value is independent of the pressure.

If both  $P^\alpha$  and  $P^\beta$  are so small that we may ignore the compressibility, then (572) simplifies to the approximate form

$$\Pi = g \frac{RT}{V_0^*} \log \frac{1}{N_0}, \quad (573)$$

where  $g$  is to be given its value in the solution at the pressure  $P^\alpha$ .

Just as for a semi-ideal solution we may say that the ratio of the actual osmotic pressure to the ideal value of the osmotic pressure is equal to the osmotic coefficient, but for a non-ideal solution we must specify that the value of the osmotic coefficient is that *at the pressure*  $P^\alpha$  at which the solution is in osmotic equilibrium in the pure solvent.

Formulae (572) and (573) may be written, in terms of the activity coefficient  $f_0$  of the solvent, in the alternative forms

$$\Pi = \frac{RT}{[V_0]} \log \frac{1}{N_0 f_0}, \quad (574.1)$$

$$\Pi = \frac{RT}{V_0^*} \log \frac{1}{N_0 f_0}, \quad (574.2)$$

where  $f_0$  is the activity coefficient of the solvent in the solution *at the pressure*  $P^\alpha$  at which it is in osmotic equilibrium with the pure solvent.

*Freezing-point.*—By reasoning exactly similar to that leading to (536), we obtain for the lowering  $\theta$  of freezing-point of a non-ideal solution

$$g \log \frac{1}{N_0} = \frac{L_F^\circ}{RT^{\circ 2}} \theta + \frac{\theta^2}{T^{\circ 2}} \left\{ \frac{L_F^\circ}{RT^\circ} - \frac{1}{2} \frac{C^L - C^S}{R} \right\}, \quad (575)$$

where  $T^\circ$  is the freezing-point of the pure solvent,  $L_F^\circ$  its molar heat of fusion at its freezing-point,  $C^L$  and  $C^S$  its molar heat capacities at constant pressure in the liquid and solid state.

Formula (575) is accurate, neglecting terms in  $\left(\frac{\theta}{T^\circ}\right)^3$ , provided  $g$  denotes the value of the osmotic coefficient of the solution *at its freezing-point*. This will, for non-ideal solutions, differ from its value at other temperatures, according to (557). It will usually be permissible to regard  $g$  in (575) as equal to the value of the osmotic coefficient in the solution at the freezing-point of the pure liquid solvent.

*Boiling-point.*—For the rise  $\theta$  of boiling-point over  $T^\circ$ , that of the pure solvent, we obtain in an exactly similar manner

$$g \log \frac{1}{N_0} = \frac{L_E^\circ}{RT^{\circ 2}} \theta + \frac{\theta^2}{T^{\circ 2}} \left\{ -\frac{L_E^\circ}{RT^\circ} - \frac{1}{2} \frac{C^L - C^G}{R} \right\}, \quad (576)$$

where  $L_E^\circ$  is the molar latent heat of evaporation of the pure solvent at its boiling-point,  $C^L$  and  $C^G$  are the molar heat capacities at constant pressure of the pure solvent in the liquid and vapour states respectively. Formula (576) is accurate, neglecting terms



in  $\left(\frac{\theta}{T^\circ}\right)^s$  provided  $g$  denotes the value of the osmotic coefficient in the solution *at its boiling-point*. This will, for a non-ideal solution, according to (557), differ from its value at any other temperature. It will usually be permissible to regard  $g$  in (576) as equal to the value of the osmotic coefficient in the solution at the boiling-point of the pure solvent.

*Solubility*.—In analogy with (540) we have for all solutions of various compositions, in a given solvent at given temperature and pressure, saturated with respect to the solid phase of pure  $s$

$$N_s f_s = \text{constant.} \quad (577)$$

In analogy with (495) we have

$$\frac{\partial \log N_s f_s}{\partial T} = \frac{L_s^\circ}{RT^2}, \quad (578)$$

where  $L_s^\circ$  is the molar heat of solution of the solid  $s$  in an infinitely dilute solution. Comparison of (578) and (552.1) leads to

$$\frac{\partial \log N_s}{\partial T} = \frac{L_s}{RT^2}, \quad (579)$$

where  $L_s$  is the molar heat of solution of the solid  $s$  in the actual saturated solution.

*Distribution between Two Solvents*.—For the equilibrium as regards the species  $s$  between two solvents  $\alpha$  and  $\beta$  we have, in analogy with (541),

$$\frac{[N_s f_s]^\beta}{[N_s f_s]^\alpha} = l_s, \quad (580)$$

where the partition coefficient  $l_s$  is for a given pair of solvents a function of the temperature and pressure only. According to (499) the dependence of  $l_s$  on the temperature is

$$\frac{\partial \log l_s}{\partial T} = \frac{L_s^\circ}{RT^2}, \quad (581)$$

where  $L_s^\circ$  denotes the molar heat of transference of  $s$  from an infinitely dilute solution in the solvent  $\alpha$  to an infinitely dilute solution in the solvent  $\beta$ . Combining (581) and (552.1), we deduce

$$\frac{\partial \log N_s^\beta / N_s^\alpha}{\partial T} = \frac{L_s}{RT^2}, \quad (582)$$

where  $L_s$  is the molar heat of transference of  $s$  from the actual solution  $\alpha$  to the actual solution  $\beta$  in equilibrium with each other as regards  $s$ .

*Law of Mass-Action.*—In analogy with (544) we obtain for the law of mass-action in non-ideal solutions

$$\frac{(N_Q f_Q)^q \cdot (N_R f_R)^r}{(N_L f_L)^l \cdot (N_M f_M)^m} = K'(T, P), \quad (583)$$

where the equilibrium constant  $K'$  is for given solvent, temperature and pressure a constant.

The dependence of  $K'$  on the temperature is, according to (502), given by

$$\frac{\partial \log K'}{\partial T} = \frac{L^\circ}{RT^2} \quad (584)$$

where  $L^\circ$  is the heat of reaction (heat absorbed when the forward reaction takes place at constant temperature and pressure) at infinite dilution in the given solvent.

Alternatively, (583) may be written

$$\frac{(N_Q)^q \cdot (N_R)^r}{(N_L)^l \cdot (N_M)^m} = K' \frac{(f_L)^l \cdot (f_M)^m}{(f_Q)^q \cdot (f_R)^r}, \quad (585)$$

If we denote either side of equation (585) by  $K_N$ , then  $K_N$  is not independent of the concentrations. Such a name as "concentration equilibrium constant" used by some writers is therefore misleading. A more appropriate name would be the "equilibrium mole-fractions product."

Comparing (584) with (552.1) we obtain for the temperature coefficient of  $K_N$

$$\frac{\partial \log K_N}{\partial T} = \frac{L}{RT^2}, \quad (586)$$

where  $L$  denotes the heat of reaction in the actual solution.

*Distinction between Solvent and Solute.*—As already mentioned, the distinction between solvent and solute is, from a thermodynamic point of view, arbitrary. All the thermodynamic formulæ obtained are independent of the choice of solvent, only the numerical values of the various functions will be affected. This is illustrated for a two component mixture in Fig. 6, where the partial vapour pressures of the two components 1 and 2 are plotted against the mole fraction of either. The partial vapour pressure curve for component 1 is represented by the full curve  $O_2P_1$ , and that for component 2 by the full curve  $O_1P_2$ . The

vapour pressures of 1 and 2 in the pure state are represented by the lengths  $O_1P_1$  and  $O_2P_2$  respectively. We shall denote these values by  $p_1^0$  and  $p_2^0$ .

Suppose now we regard the species 1 as solvent. The ideal laws are then for the solvent (species 1) Raoult's Law (471)—

$$p_1 = p_1^0 N_1, \quad (587)$$

represented by the dotted straight line  $O_2P_1$ ; and for the solute (species 2) by Henry's Law (466)—

$$p_2 = k_2 N_2, \quad (588)$$

represented by the dotted line  $O_1Q_1$ . The value of  $k_2$  is then represented by the length  $O_2Q_1$ . For either component the value of the activity coefficient is the ratio of the actual vapour pressure given by the full curves to the ideal vapour pressure given by the dotted straight lines. It is to be noticed that both activity coefficients have the value unity for compositions approaching pure species 1 and that deviations from unity become appreciable for both components at the same mole fraction.

If, on the other hand, we choose to regard species 2 as solvent, the ideal laws are for species 2 Raoult's Law (471)—

$$p_2 = p_2^0 N_2 \quad (589)$$

represented by the broken straight line  $O_1P_2$ ; and for species 1 Henry's Law (466)—

$$p_1 = k_1 N_1, \quad (590)$$

represented by the broken straight line  $O_2Q_2$ , the value of  $k_1$  being represented by the length  $O_1Q_2$ . The activity coefficient of either component is equal to the ratio of the actual vapour pressure given by the full curves to the ideal vapour pressure given by the broken straight lines. With this convention both activity coefficients have the value unity for compositions

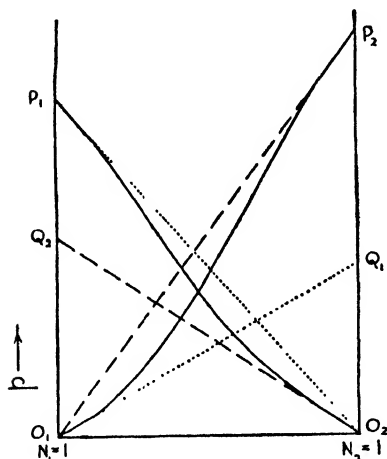


FIG. 6.

approaching pure 2 and deviations from unity become appreciable for both activity coefficients at the same mole fraction.

Either of the two choices described above will lead to the same physical results when the thermodynamic formulæ of this chapter are applied. In passing from the first system to the second the value of  $f_1$  for each composition is altered in the ratio  $\frac{p_1^\circ}{k_1}$ , while that of  $f_2$  is altered throughout in the ratio  $\frac{k_2}{p_2^\circ}$ . The values of other constants, such as  $k$  in the vapour pressure formula (562),  $l$  in the distribution formula (580),  $K'$  in the law of mass-action (583), and the solubility constant in (577) will be correspondingly altered, but their independence of the composition remains unaffected.

If preferred, one need not regard any species as solvent more than any other, but treat all species on an equal footing. In this case, for each species  $i$  one may define the activity coefficient  $f_i$  by

$$\mu_i = \mu_i^\circ(T_1P) + RT \log N_i f_i, \quad (591.1)$$

where

$$f_i \rightarrow 1, \quad \text{when } N_i \rightarrow 1, \quad N_j \rightarrow 0. \quad (591.2)$$

We then obtain for the partial vapour pressure  $p_i$  of each species  $i$

$$p_i = p_i^\circ N_i f_i. \quad (592)$$

where  $p_i^\circ$  is the vapour pressure of  $i$  in the pure state. With this convention all the physical laws given by the formulæ of the present chapter will be unaltered. The values of such constants as  $l_i$ ,  $K'$  will be altered, but their independence of the composition will be unaffected. In Fig. 6 the value of  $f_1$  in this case is the ratio of the actual partial vapour pressure of 1 given by the full curve  $O_2P_1$  to the ideal value given by the *dotted* straight line  $O_2P_1$ . But  $f_2$  is the ratio of the value of  $O_1P_2$  given by the full curve  $O_1P_2$  to that given by the *broken* straight line  $O_1P_2$ .

## NOTES AND REFERENCES

*Activity Coefficient.*—The use of the activity coefficient as a purely thermodynamic function is due to G. N. Lewis, *vide* Lewis and Randall's "Thermodynamics". The definition given here is in exact agreement with that given by Debye in *Phys. Z.*, **25**, 97 (1924). Alternative definitions not exactly equivalent to that given here are used by both Lewis himself and other authors. These other definitions have the disadvantage that even for an ideal solution the activity coefficient is not unity except at extreme dilutions. This remark is amplified in Chapter IX.

The use of  $f_i$  to denote an activity coefficient is in conformity with the

notation used by Brönsted, and widely used by other authors. Lewis and certain other American authors use  $\gamma_i$  for the activity coefficient and  $f_i$  for the fugacity.

*Activity.*—A function called the "activity" of the species  $i$ , and denoted by  $a_i$  is defined by G. N. Lewis by the relation

$$\mu_i - \mu_i^S = RT \log a_i,$$

where  $\mu_i^S$  denotes the value of  $\mu_i$  in some standard state *at the same temperature and same pressure*.

When considering variations of temperature and pressure the activity is an awkward function to use because the standard state itself varies with temperature and pressure. It is therefore only when considering variations at constant temperature and pressure that the activity might be useful. But for such variations of composition at constant temperature and pressure in any given solvent

$$D\mu_i = RTD \log N_i f_i,$$

and there seems nothing to be gained by the introduction of a separate function  $a_i$  which is simply proportional to the product  $N_i f_i$ , and whose absolute value is of no significance, but requires for its definition the choice of an arbitrary standard state.

If one is interested in comparing the properties of an actual solution with those of an ideal solution, then the activity coefficient  $f_i$  provides a useful measure of the degree of non-ideality. This is the reason for the introduction of the activity coefficient. If, on the other hand, one is not interested in ideal solutions, but prefers to consider the equilibrium properties of any actual solution from a purely thermodynamic non-molecular standpoint, then the natural function to use is the chemical potential  $\mu_i$ , and there seems nothing to be gained by introducing yet another subsidiary function  $a_i$  defined by the equation given above.

*Osmotic Coefficient.*—This function was first introduced by Bjerrum in *Fysisk Tidsskrift*, **15**, 66 (1916) [German translation in *Z. El. Chem.*, **24**, 325 (1918)]. Its relationship to the activity coefficients of the solute species is given by Bjerrum in this paper and again in greater detail in *Z. Physikal. Chem.*, **104**, 406 (1923). Just as in the case of the activity coefficient, various definitions are in use which are equivalent to one another only at extreme dilutions. The definition given here is chosen so that in an ideal solution the osmotic coefficient is always unity whatever the concentrations. Any deviation of the osmotic coefficient from unity is thus a measure of the deviation from ideality.

*Osmotic Pressure.*—The exact and yet compact formulæ (531) and (572) for the osmotic pressure of the most general semi-ideal or non-ideal solution are due to Donnan and Guggenheim, *Z. Physikal. Chem.*, A, **162**, 346, 1932.

## CHAPTER IX

### EXTREMELY DILUTE NON-IDEAL SOLUTIONS AND EXTREMELY DILUTE IDEAL SOLUTIONS

*Significance of Extremely Dilute Solutions.*—As already mentioned, solutions of non-electrolytes often remain ideal up to concentrations of the order  $N_s = 10^{-2}$ , sometimes even up to  $N_s = 1$  in the case of perfect solutions. In order not to mask this regularity of behaviour it is important not to use inexact forms for the ideal laws. For solutions of electrolytes, on the other hand, measurable deviations from ideality occur at much lower concentrations,  $N_s = 10^{-6}$  or less. In performing calculations for such non-ideal dilute solutions, it is often convenient to use formulæ different from the accurate formulæ of Chapters VII and VIII, but differing inappreciably from them as long as every  $N_s$  is very small compared with  $N_0$  or with unity. Such a solution may conveniently be called "extremely dilute". It is to be observed that the property of "extreme diluteness" is one depending, not on the physical properties of the solution, but purely on the relative quantities of solute and solvent. What concentration to choose as upper limit depends, of course, on the accuracy aimed at. For 1 per cent. accuracy one would generally be safe in choosing  $N_s = 10^{-2}$  (this corresponding to concentrations of one-half mole per litre in water). A solution of a non-electrolyte may well continue to be ideal when it is no longer "extremely dilute," whereas a solution of a strong electrolyte will cease to be ideal at concentrations some thousand times less than the upper limit of "extreme dilution". The properties of ideality and "extreme dilution" are independent, except that both hold in the neighbourhood of infinite dilution.

*Concentration Scales.*—There are several scales of concentration in more general use than the mole fraction scale, which is the scale on which the laws of ideal solution take a simple form. The two most important of these are those known as the "molality" scale and the "volume concentration" scale.

Let  $n_s$  denote the number of moles of the solute species  $s$ , and  $n_0$  the number of moles of the solvent in a volume  $V$  of

solution. Then the mole fraction  $N_s$  of each solute  $s$  and the mole fraction  $N_0$  of the solvent are defined by

$$N_s = \frac{n_s}{n_0 + \sum_s n_s}, \quad (593.1)$$

$$N_0 = 1 - \sum_s N_s. \quad (593.2)$$

The "molality"  $m_s$  of each solute species  $s$  is defined by

$$m_s = \frac{n_s}{M_0 n_0} = \frac{N_s}{M_0 N_0}, \quad (593.3)$$

where  $M_0$  is the molar mass ("molecular weight") of the solvent (expressed in kilograms per mole).

The "volume concentration"  $C_s$  of each solute species  $s$  is defined by

$$C_s = \frac{n_s}{V} = \frac{N_s}{N_0 V_0 + \sum_s N_s V_s}, \quad (593.4)$$

where the unit of volume is the litre.

For extremely dilute solutions the values of  $M_0 N_0$  the denominator in the last member of (593.3) has practically the same value  $M_0$  as it has for the pure solvent. Similarly, the denominator  $N_0 V_0 + \sum_s N_s V_s$  of the last member of (593.4) has practically the constant value  $V_0$  the molar volume of the pure solvent. It follows that for extremely dilute solutions in a given solvent at a given temperature and pressure

$$m_s \propto C_s \propto N_s. \quad (593.5)$$

*Chemical Potential of Solute.*—From the proportionality relations (593.5) it follows that in place of the exact formula (550) we may for extremely dilute solutions use one of the approximate formulæ

$$\mu_s = \mu_s^{\circ'}(T, P) + RT \log m_s f_s, \quad (594.1)$$

$$\mu_s = \mu_s^{\circ''}(T, P) + RT \log C_s f_s, \quad (594.2)$$

where  $\mu_s^{\circ}$ ,  $\mu_s^{\circ'}$ ,  $\mu_s^{\circ''}$  will differ only by a term proportional to the temperature  $T$ . Most authors prefer to use one of the formulæ (594.1) or (594.2) as definition of the activity coefficient  $f_s$ . The objection to this procedure is that according to either of these definitions the activity coefficients  $f_s$  will differ from unity even in an ideal solution unless it happens to be extremely

dilute. It will then no longer be allowable to regard  $1 - f_s$  or  $\log f_s$  as a measure of deviations from ideality. Thus the activity coefficient defined in either of these alternative manners would be deprived of the very property to which it owes its usefulness.

*Chemical Potential of Solvent.*—For extremely dilute solutions formula (554) for the chemical potential of the solvent can be put into the approximate form

$$\mu_0 = \mu_0^\circ(T, P) - gRT \sum_s N_s, \quad (595.1)$$

since approximately

$$\begin{aligned} \log N_0 &= \log(1 - \sum_s N_s) \\ &= - \sum_s N_s. \end{aligned}$$

To a like degree of approximation we may, instead of (554), write

$$\mu_0 = \mu_0^\circ(T, P) - gRT M_0 \sum_s m_s, \quad (595.2)$$

where  $M_0$  is the molar mass of the solvent in units of 1000 grammes and  $m_s$  is the molality of the solute  $s$ . Similarly, we may write

$$\mu_0 = \mu_0^\circ(T, P) - gRT V_0^\circ \sum_s C_s, \quad (595.3)$$

where  $V_0^\circ$  is the molar volume of the pure solvent (expressed in litres per mole).

*Approximate Relations.*—By making use of the approximations just described, the various formulæ of the last two chapters can be expressed in alternative forms which may sometimes be more convenient and for extremely dilute solutions will be sufficiently accurate. It cannot be too strongly emphasised that these formulæ are not applicable to solutions that are not extremely dilute.

We shall merely list the approximate relations corresponding to the use of the volume concentration scale which are analogous to formulæ (594.2) and (595.3). It will be evident that there is a similar set of approximate relations analogous to (594.1) and (595.2) in which the molality scale is used.

*Vapour Pressure of Solute.*—For the vapour pressure of the solute  $s$  in place of (528) or (562) we have the approximate formula

$$p_s = k' C_s f_s, \quad (596)$$

where  $k'$  is independent of the concentrations.



*Distribution of Solute between Two Solvents.*—For the distribution of the solute  $S$  between two immiscible solvents  $\alpha$  and  $\beta$ , we have, in place of (541) and (580), the approximate formula

$$\frac{[C_S f_S]^\beta}{[C_S f_S]^\alpha} = l'_S, \quad (597)$$

where  $l'_S$  is independent of the concentrations.

*Law of Mass-Action.*—For the law of mass action we have, in place of (544) or (583), the approximate formula

$$\frac{(C_Q f_Q)^q \cdot (C_R f_R)^r}{(C_L f_L)^l \cdot (C_M f_M)^m} = K'', \quad (598)$$

where  $K''$  is independent of the concentrations.

The quantity  $K_C$  defined by

$$K_C \equiv \frac{(C_Q)^q (C_R)^r}{(C_L)^l \cdot (C_M)^m}, \quad (599)$$

is referred to by some authors as the "concentration equilibrium constant," an unfortunate terminology, for  $K_C$  is not a "constant" at all but varies with the concentrations according to

$$K_C = K'' \frac{(f_L)^l \cdot (f_M)^m}{(f_Q)^q \cdot (f_R)^r}. \quad (600)$$

A more suitable name for  $K_C$  is the "equilibrium concentrations function" or the "equilibrium concentrations product".

*Vapour Pressure of Solvent.*—For the vapour pressure  $p_0$  of the solvent we have, in place of (529) or (567), the approximate formula

$$\frac{p_0^\circ - p_0}{p_0^\circ} = g V_0^\circ \sum_S C_S, \quad (601)$$

where  $p_0$  is the vapour pressure of the solvent in the solution and  $p_0^\circ$  its vapour pressure in the pure state.

*Lowering of Freezing-point and Rise of Boiling-point.*—For the lowering of freezing-point and rise of boiling-point we have instead of (537), (539), or (575), (576) the approximate formulæ

$$\frac{L_F^\circ}{V_0^\circ R T^{\circ 2}} \theta = g \sum_S C_S, \quad (602)$$

$$\frac{L_B^\circ}{V_0^\circ R T^{\circ 2}} \theta = g \sum_S C_S. \quad (603)$$

*Osmotic Pressure.*—For the osmotic pressure  $\Pi$  we have, in place of (532.3) or (573), the approximate formula

$$\Pi = gRT \sum_s C_s. \quad (604)$$

*Relation between Osmotic Coefficient and Activity Coefficients.*—For variations in composition at given temperature and pressure the relation (559.2) between variations of the activity coefficients  $f_s$  of the solute species  $s$  and the osmotic coefficient  $g$  of the solvent may be put into the approximate form

$$- \sum_s C_s d g + (1 - g) \sum_s d C_s + \sum_s C_s d \log f_s = 0. \quad (606)$$

In the simple case of only one solute species (606) becomes

$$d \log f_s = d g - (1 - g) d \log C_s. \quad (607)$$

This may be written in the integral form

$$- \log f_s = (1 - g) + \int_{C_s=0}^{C_s} (1 - g) d \log C_s. \quad (608)$$

If one has determined the osmotic coefficient  $g$  as a function of  $C_s$ , for example by freezing-point measurements at various concentrations, formula (608) enables one by very simple calculation to determine the dependence of  $f_s$ , the activity coefficient of the solute, on the concentration  $C_s$ .

If, in particular,  $1 - g$  is proportional to the concentration  $C_s$  to the power  $r$ , that is to say

$$1 - g = \alpha(C_s)^r, \quad (609)$$

where  $\alpha$  is independent of the concentration  $C_s$ , then (608) leads to the formula for

$$\begin{aligned} - \log f_s &= \frac{r+1}{r} \alpha(C_s)^r \\ &= \frac{r+1}{r} (1 - g). \end{aligned} \quad (610)$$

Formula (610), due to Bjerrum, shows that the quantity  $(1 - g)$  is of the same order of magnitude as  $\log f_s$ . As already mentioned in Chapter VII, it is for this reason that  $1 - g$  is a more convenient measure of deviations from ideality than the quantity  $\log f_0$ , which often has an inconveniently small numerical value.

*Extremely Dilute Ideal Solutions.*—The formulæ for solutions at once extremely dilute and ideal are obtained by merely setting

$$f_s = 1, \quad (611.1)$$

$$g = 1, \quad (611.2)$$

in the laws of extremely dilute non-ideal solutions. These laws of extremely dilute ideal solutions are due to van't Hoff, who realised their limitations. They have unfortunately only too frequently been applied under conditions for which they do not and were not meant to hold.

In particular, the formula for the osmotic pressure  $\Pi$  in a solution that is both ideal and extremely dilute takes the form

$$\Pi = RT \sum_s C_s, \quad (612)$$

of the same type as the formula (325) for the pressure of a perfect gaseous mixture. This formula, however, departs widely from the exact formula (475) for ideal solutions at high concentrations.

#### NOTES AND REFERENCES

*Osmotic Coefficient.*—The relation between the osmotic coefficient of the solvent and the activity coefficient of the solute species in extremely dilute solutions was given by Bjerrum in *Fysisk Tidsskrift*, **15**, 66 (1916) [German translation in *Z. El. Chem.*, **214**, 325 (1918)]; and again in greater detail in *Z. Physikal. Chem.*, **104**, 406 (1923). An equivalent treatment is given in Lewis and Randall's "Thermodynamics". The function there denoted by  $j$  is for extremely dilute solutions identical with  $1 - g$ .

## CHAPTER X

### ELECTRO-CHEMICAL SYSTEMS

*Electro-chemical Potentials.*—It will be remembered that the chemical potentials  $\mu_i$  were originally defined by equation (19)

$$\mu_i^\alpha = \left( \frac{\partial E^\alpha}{\partial n_i^\alpha} \right)_{S^\alpha, V^\alpha, n_j^\alpha} \quad (613)$$

From this equation was deduced, inter alia, the formula (28)

$$dG^\alpha = -S^\alpha dT^\alpha + V^\alpha dP^\alpha + \sum_i \mu_i^\alpha dn_i^\alpha, \quad (614)$$

which serves as a starting-point for the consideration of most types of equilibrium. These equations hold for any type of component species, including species with electrical charges (ions). We shall, however, in the case of ions use the symbol  $\bar{\mu}_i$  instead of  $\mu_i$  and shall call the  $\bar{\mu}_i$  the "electro-chemical potentials" of the ions. We do this to emphasise the fact that their values depend not only on the composition of the phase, but also on its electrical state.

The last statement requires some amplification; for if the composition of a phase is given exactly (i.e. the exact number of moles of each species present), then its electrical state is also determined, since "electricity" apart from matter is a mathematical fiction, the realities being charged ions, including electrons. However, the magnitude of the charge on any ion is so great that in order to charge a phase of any macroscopic dimensions to even the highest potentials realisable, the necessary alteration of the composition of the system is entirely negligible. It is owing to this very important fact that we may speak of two phases of "identical" chemical composition in different electrical states.

*Phases of Identical Composition.*—The difference of the electro-chemical potential  $\bar{\mu}_i$  of an ion  $i$  between two phases of "identical" composition will clearly be proportional to the electric charge of the ion in question and independent of its chemical nature. We may thus in this case write

$$\bar{\mu}_i^\beta - \bar{\mu}_i^\alpha = Q_i(\psi^\beta - \psi^\alpha), \quad (615)$$

where  $Q_i$  is the charge of the species  $i$  and  $(\psi^\beta - \psi^\alpha)$  is called the "electric potential difference" between  $\alpha$  and  $\beta$ .

Since the charge of one mole of any ion is a small integral multiple of a unit charge, called the "Faraday," we have

$$Q_i = z_i \mathcal{F}, \quad (616)$$

where  $\mathcal{F}$  denotes the Faraday and  $z_i$  is a small positive or negative integer, called the "valency" of the ion. Substituting (616) into (615), we have for the difference of electric potentials between two phases  $\alpha$  and  $\beta$  of identical composition,

$$\psi^\beta - \psi^\alpha = \frac{1}{z_i \mathcal{F}} (\bar{\mu}_i^\beta - \bar{\mu}_i^\alpha). \quad (617)$$

This equation defines the electric potential difference between two phases of identical composition in terms of the difference in the values of the electro-chemical potential of any ionic species.

*Phases of Different Composition.*—For two phases of different composition no such simple relation as (617) exists. It is, however, usual to write formally

$$\begin{aligned} \bar{\mu}_i^\beta - \bar{\mu}_i^\alpha &= \mu_i^\beta - \mu_i^\alpha + z_i \mathcal{F} (\psi^\beta - \psi^\alpha) \\ &= (\mu_i^\beta + z_i \mathcal{F} \psi^\beta) - (\mu_i^\alpha + z_i \mathcal{F} \psi^\alpha), \end{aligned} \quad (618)$$

where  $\mu_i$  represents the "purely chemical" part of the electro-chemical potential and  $z_i \mathcal{F} \psi$  the "purely electrical" part of the electro-chemical potential. Since, however, all equilibria are determined entirely by the quantities  $\bar{\mu}_i$ , the electro-chemical potentials, such a decomposition into two terms is in general arbitrary and of no thermodynamic significance. For no thermodynamic measurements could give any information concerning the separate terms  $\mu_i$  and  $z_i \mathcal{F} \psi$ , but only concerning their sum. Whether this separation of  $\bar{\mu}_i$  into two parts has any physical significance in non-thermodynamic considerations will not be discussed here.

Of course,  $\bar{\mu}_i$  itself, like  $\mu_i$  for an uncharged species, is indefinite to the extent of an additive term of the form  $(a + bT)$ , depending on the arbitrarily chosen zero for  $E$  and  $S$ . But its difference  $\Delta \bar{\mu}_i$  between two phases at the same temperature is completely defined, whereas  $\Delta \mu_i$  and  $\Delta \psi$  are in general indefinite, even for two phases at the same temperature.

*Purely Chemical Processes.*—In most ordinarily occurring thermodynamic processes the net electric charge transferred from one phase to another is zero. It will be convenient to refer to

such processes as "purely chemical". This is expressed by the condition

$$\sum_i \lambda_i z_i = 0, \quad (619)$$

where  $\lambda_i$  is the number of moles of type  $i$  transferred. [For convenience we suppose the sum under the  $\sum$  to include any uncharged species for which  $z_i = 0$ .] For such a process the increase of the Gibbs free energy  $G$ , which is the function of most importance for the study of equilibria at constant temperature and pressure, is given by

$$\Delta G = \sum_i \lambda_i \Delta \bar{\mu}_i. \quad (620)$$

According to (618) this may be written formally

$$\Delta G = \sum_i \lambda_i \Delta \mu_i + \sum_i \lambda_i z_i \mathcal{F} \Delta \psi. \quad (621)$$

But by (619) the second term on the right vanishes, and there remains

$$\Delta G = \sum_i \lambda_i \Delta \mu_i. \quad (622)$$

Thus, although the individual  $\mu_i$  are not defined any sum of the form  $\sum_i \lambda_i \mu_i$  is defined, provided the  $\lambda_i$  satisfy the condition (619).

As long as we are dealing with "purely chemical" processes, we may write indifferently  $\mu_i$  or  $\bar{\mu}_i$ . It will be convenient to refer to equilibria corresponding to purely chemical processes as "purely chemical" equilibria.

*Ideal Dilute Solutions of Ions.*—In the limit of very high dilutions solutions of ions behave in a simple manner analogous to other ideal solutions. This simple behaviour can be expressed in the form that for two such solutions  $\alpha$  and  $\beta$  in the same solvent at the same temperature and pressure

$$\bar{\mu}_i^\beta - \bar{\mu}_i^\alpha = RT \log \frac{N_i^\beta}{N_i^\alpha} + z_i \mathcal{F} (\chi^\beta - \chi^\alpha), \quad (623)$$

where  $\chi^\beta - \chi^\alpha$  has the same value for any ionic species  $i$ . The value of  $\chi^\beta - \chi^\alpha$  depends on both the composition and the electrical state of the two phases  $\alpha$  and  $\beta$ . Comparison of (623) with the corresponding formula

$$\mu_u^\beta - \mu_u^\alpha = RT \log \frac{N_u^\beta}{N_u^\alpha}, \quad (624)$$

for an electrically neutral species  $u$ , suggests a natural method of splitting the electrochemical potential  $\bar{\mu}_i$  into a chemical term  $\mu_i$  and an electrical term  $z_i \mathcal{F} \psi$  for ideal solutions in a given solvent. We define the chemical potential  $\mu_i$  of the ionic species  $i$  in an ideal solution by

$$\mu_i^\beta - \mu_i^\alpha = RT \log \frac{N_i^\beta}{N_i^\alpha}, \quad (625)$$

and then the electric potential difference  $\psi^\beta - \psi^\alpha$  between the two phases is defined by

$$\psi^\beta - \psi^\alpha = \chi^\beta - \chi^\alpha = \frac{1}{z_i \mathcal{F}} \left\{ \bar{\mu}_i^\beta - \bar{\mu}_i^\alpha - RT \log \frac{N_i^\beta}{N_i^\alpha} \right\}, \quad (626)$$

where all the quantities on the right side have a direct physical significance.

*Non-Ideal Solutions of Ions in Given Solvent.*—For a solution of ions that is not ideal we may formally introduce ionic activity coefficients by the relation

$$\mu_i^\beta - \mu_i^\alpha = RT \log \frac{N_i^\beta f_i^\beta}{N_i^\alpha}, \quad (627)$$

where the phase  $\alpha$  is a solution in the same solvent sufficiently dilute to be ideal. Since, however, the quantities  $\mu_i^\beta$  are arbitrary to the extent of a term of the form  $z_i \chi^\beta$  where  $\chi^\beta$  is an arbitrary function of the concentrations, the same applies to  $RT \log f_i^\beta$ . When, however, we consider a purely chemical process or equilibrium the  $\log f_i$  will occur in a combination of the form

$$\sum_i \lambda_i \log f_i, \quad (628)$$

where the  $\lambda_i$  satisfy (619), and so the arbitrary additive terms disappear.

In particular, for a salt consisting of  $q_+$  positive ions of valency  $z_+$  and  $q_-$  negative ions of valency  $z_-$ , the condition of electrical neutrality of the salt is

$$q_+ z_+ + q_- z_- = 0. \quad (629)$$

It follows that the quantity  $f_\pm$  defined by

$$(f_\pm)^{q_+ + q_-} = (f_+)^{q_+} \cdot (f_-)^{q_-} \quad (630)$$

is quite definite, although the value of either  $f_+$  or  $f_-$  is entirely arbitrary.  $f_\pm$  is called the "mean activity coefficient" of the salt. Another example of a combination of ionic activity

coefficients that is quite definite is the ratio of the activity coefficients of two ions of the same valency.

*Ideal Dilute Solutions in Different Solvents.*—For two ideal dilute solutions of ions in different solvents  $\alpha$  and  $\beta$  at the same temperature and pressure, we may write formally in analogy with solutions of uncharged species

$$\mu_i^\beta - \mu_i^\alpha = RT \log \frac{N_i^\beta}{N_i^\alpha} - RT \log l_i, \quad (631)$$

where  $l_i$  is the "ionic partition coefficient". But  $RT \log l_i$  like  $(\mu_i^\beta - \mu_i^\alpha)$  will be arbitrary to the extent of an additive term of the form  $z_i(\chi^\beta - \chi^\alpha)$ , where in each solvent an arbitrary value may be assigned to  $\chi$ . Nevertheless, such linear combinations of the  $\log l_i$  as correspond to "purely chemical" equilibria will be definite. For instance, for a salt of  $q_+$  positive ions of valency  $z_+$  and  $q_-$  negative ions of valency  $z_-$  owing to the condition of neutrality

$$q_+ z_+ + q_- z_- = 0, \quad (632)$$

the quantity

$$q_+ \log l_+ + q_- \log l_- \quad (633)$$

is definite and so also the "mean partition coefficient"  $l_\pm$  of the salt defined by

$$(l_\pm)^{q_+ + q_-} = (l_+)^{q_+} \cdot (l_-)^{q_-}, \quad (634)$$

although the individual ionic partition coefficients  $l_+$ ,  $l_-$  are indefinite. Similarly, the ratio of the partition coefficients of the two ions of the same charge is definite.

*Electric Potential Difference.*—To recapitulate, the separation of the difference in two phases of the electro-chemical potential  $\bar{\mu}_i$  into a purely chemical part  $\mu_i$  and a purely electrical part  $z_i \mathcal{F} \psi$  is thermodynamically defined in only two cases:—

(a) for two phases of identical composition when  $\mu_i$  is the same in both phases, and so  $\Delta \psi$  is defined by

$$z_i \mathcal{F} \Delta \psi = \Delta \bar{\mu}_i, \quad (635)$$

(b) for two ideal solutions in the same solvent, when  $\Delta \mu_i$  is conventionally defined by

$$\Delta \mu_i = RT \Delta \log N_i, \quad (636)$$

and so  $\Delta \psi$  is defined by

$$z_i \mathcal{F} \Delta \psi = \Delta \bar{\mu}_i - RT \Delta \log N_i. \quad (637)$$



Nevertheless, if convenient, we may calculate with ionic potentials, ionic activity coefficients and ionic partition coefficients, as the arbitrariness will vanish from any result of physical significance.

*Solubility of Electrolytes.*—All solutions at a given temperature and pressure saturated with respect to the solid phase of an electrolyte yielding  $q_+$  cations of valency  $z_+$  and  $q_-$  anions of valency  $z_-$  must satisfy the condition

$$q_+ \bar{\mu}_+ + q_- \bar{\mu}_- = \text{constant}, \quad (638)$$

where  $\bar{\mu}_+$ ,  $\bar{\mu}_-$  denote the electro-chemical potentials of the cation and of the anion. Formally, we may for a given solvent in accordance with (627), write in place of (638),

$$q_+ \{RT \log N_+ + RT \log f_+ + z_+ \mathcal{F} \psi\} \\ + q_- \{RT \log N_- + RT \log f_- + z_- \mathcal{F} \psi\} = \text{constant}. \quad (639)$$

But, according to the condition of electro-neutrality of the solid electrolyte,

$$q_+ z_+ + q_- z_- = 0, \quad (640)$$

and (639) therefore simplifies to

$$q_+ \{\log N_+ + \log f_+\} + q_- \{\log N_- + \log f_-\} = \text{constant}. \quad (641)$$

Introducing the mean activity coefficient, this becomes

$$q_+ \log N_+ + q_- \log N_- + (q_+ + q_-) \log f_{\pm} = \text{constant}, \quad (642)$$

or

$$(N_+)^{q_+} \cdot (N_-)^{q_-} \cdot (f_{\pm})^{q_+ + q_-} = \text{constant}. \quad (643)$$

*Vapour Pressure of Electrolyte.*—Suppose an electrically neutral species is undissociated in the gaseous state, but in solution each mole yields  $q_+$  cations of valency  $z_+$  and  $q_-$  anions of valency  $z_-$ . Then the condition for equilibrium between the solution  $\alpha$  and the vapour phase  $\beta$  is

$$q_+ \bar{\mu}_+^{\alpha} + q_- \bar{\mu}_-^{\alpha} = \mu_u^{\beta}, \quad (644)$$

where the suffix  $u$  refers to the undissociated molecules. Using the condition of electro-neutrality (629), formula (630) for the mean activity coefficient and formula (321) for the chemical potential of a perfect gas, we deduce from (644) the equilibrium condition for constant temperature, pressure and solvent

$$p_u \propto (N_+)^{q_+} \cdot (N_-)^{q_-} \cdot (f_{\pm})^{q_+ + q_-}. \quad (645)$$

*Mean Activity Coefficients.*—The two equilibria last considered must suffice as typical examples, showing that all purely chemical equilibria can be expressed in terms of the mean activity coefficients. The ionic activity coefficients always occur in such combinations as can be expressed in terms of the mean activity coefficients.

We now pass to the consideration of some equilibria that are not purely chemical.

*Membrane Equilibria (Non-Osmotic).*—Suppose two solutions  $\alpha$  and  $\beta$  at the same temperature and pressure in the same solvent be separated by a membrane permeable to some ions, but not to others, nor to the solvent. Then, for the permeant ions we have the equilibrium conditions

$$\bar{\mu}_i^\beta = \bar{\mu}_i^\alpha. \quad (646)$$

In this case, we may not replace the  $\bar{\mu}_i$  by the  $\mu_i$ , since the process to which the equilibrium corresponds is the passage of the single ionic species  $i$  from the one phase to the other. If, however, we combine equations (646) for the  $q_+$  cations of valency  $z_+$  and  $q_-$  anions of valency  $z_-$  of a salt, we obtain

$$q_+\mu_+^\beta + q_-\mu_-^\beta = q_+\mu_+^\alpha + q_-\mu_-^\alpha, \quad (647)$$

in which it is no longer necessary to distinguish between  $\bar{\mu}_i$  and  $\mu_i$ . In terms of activity coefficients the relation (647) becomes

$$(N_+^\beta)^{q_+} \cdot (N_-^\beta)^{q_-} \cdot (f_\pm^\beta)^{q_+ + q_-} \\ = (N_+^\alpha)^{q_+} \cdot (N_-^\alpha)^{q_-} \cdot (f_\pm^\alpha)^{q_+ + q_-}. \quad (648)$$

There exists no relation defining an electric potential difference between the two phases.

Only if the solutions are ideal then  $(\mu_i^\beta - \mu_i^\alpha)$  is defined by (625), and (646) becomes

$$z_i \mathcal{F}(\psi^\beta - \psi^\alpha) = RT \log \frac{N_i^\alpha}{N_i^\beta}, \quad (649)$$

a relation due to Donnan.

For the case of a membrane separating two solutions  $\alpha$  and  $\beta$  in different solvents at the same temperature and pressure, permeable to some of the ions but impermeable to others and the solvents, the condition of equilibrium for ions of type  $i$  is still

$$\bar{\mu}_i^\beta = \bar{\mu}_i^\alpha. \quad (650)$$

In this case, even if the solutions are ideal, no relation is obtainable involving the electric potential difference separately. Formally we may instead of (650) write for two ideal solutions

$$RT \log \frac{N_i^\beta}{N_i^\alpha} = RT \log l_i - Z_i \mathcal{F}(\psi^\beta - \psi^\alpha), \quad (651)$$

but  $RT \log l_i$  and  $Z_i \mathcal{F}(\psi^\beta - \psi^\alpha)$  are both indeterminate to the extent of an arbitrary additive constant; only their sum is physically determinate.

For two ions  $i$  and  $k$  of the same valency, however, we obtain, by subtracting the two equations of the form (651),

$$\frac{N_i^\beta}{N_i^\alpha} \frac{N_k^\alpha}{N_k^\beta} = \frac{l_i}{l_k}, \quad (652)$$

where  $\frac{l_i}{l_k}$ , the "partition coefficient ratio," is physically definite and independent of the electrostatic state of the phases.

*Membrane Equilibrium (Osmotic).*—In the preceding section we assumed that the membrane was impermeable to the solvent or solvents. The more usual case of a membrane permeable to the solvent is considerably less simple. In this case equilibrium between the two phases separated by the membrane, as regards the solvent, will generally require a pressure difference between the two phases (osmotic pressure difference), and this pressure difference complicates the conditions of equilibrium for the solute ions. We shall consider only the case of one and the same solvent on both sides of the membrane.

The conditions for membrane equilibrium can still be written in the general form

$$\mu_0^\beta = \mu_0^\alpha \quad (653)$$

for the solvent, and

$$\bar{\mu}_i^\beta = \bar{\mu}_i^\alpha \quad (654)$$

for each permeant ionic species.

The chemical potential  $\mu_0$  of the solvent species is according to (553.3) given by

$$\mu_0 = \mu_0^*(T) + PV_0^*(1 - \frac{1}{2}\kappa_0 P) + RT \log N_0 f_0, \quad (655)$$

where  $\mu_0^*$ ,  $V_0^*$  and  $\kappa_0$  are for the given solvent functions of the temperature only. Similarly, for the electrochemical potential  $\bar{\mu}_i$  of a solute ionic species  $i$  we may analogously write formally

$$\begin{aligned} \bar{\mu}_i = \mu_i^*(T) + PV_i^*(1 - \frac{1}{2}\kappa_i P) + RT \log N_i \\ + RT \log f_i + z_i \mathcal{F} \psi, \end{aligned} \quad (656)$$

where  $\mu_i^*$ ,  $V_i^*$ ,  $\kappa_i$  are for the given solvent and solute functions of the temperature only.  $V_i^*$  is, in fact, the value of  $V_i$  at infinite dilution and zero pressure, while  $V_i^*(1 - \kappa_i P)$  is the value of  $V_i$  at infinite dilution at the given pressure. As explained (p. 134), we cannot measure separately the two last terms on the right of (656).

Substituting (655) and (656) respectively into (653) and (654), and introducing the symbols  $[V_0]$  and  $[V_i]$  respectively for the values of  $V_0$  and  $V_i$  at infinite dilution and at a pressure equal to the mean of the pressures  $P^\alpha$  and  $P^\beta$  on the two phases, we obtain

$$(P^\alpha - P^\beta)[V_0] = RT \log \frac{N_0^\beta f_0^\beta}{N_0^\alpha f_0^\alpha}, \quad (657)$$

$$(P^\alpha - P^\beta)[V_i] = RT \log \frac{N_i^\beta}{N_i^\alpha} + RT \log \frac{f_i^\beta}{f_i^\alpha} + z_i \mathbf{F}(\psi^\beta - \psi^\alpha), \quad (658)$$

in which, however, the last three terms on the right cannot be measured separately.

If, however, we compare formula (658) for two ionic species  $i$  and  $k$  of the same electric type, we can eliminate  $\psi^\beta - \psi^\alpha$  and obtain

$$(P^\alpha - P^\beta)([V_i] - [V_k]) = RT \log \frac{N_i^\beta N_k^\alpha}{N_k^\beta N_i^\alpha} + RT \log \frac{f_i^\beta f_k^\alpha}{f_k^\beta f_i^\alpha}. \quad (659)$$

Finally, we can eliminate  $P^\alpha - P^\beta$  from (657) and (659), and so obtain

$$\frac{N_i^\beta N_k^\alpha}{N_k^\beta N_i^\alpha} \cdot \frac{f_i^\beta f_k^\alpha}{f_k^\beta f_i^\alpha} = \left( \frac{N_0^\beta}{N_0^\alpha} \cdot \frac{f_0^\beta}{f_0^\alpha} \right)^r, \quad (660.1)$$

where  $r$  is defined by

$$r = \frac{[V_i] - [V_k]}{[V_0]}. \quad (660.2)$$

As the ionic species  $i$  and  $k$  are of the same electric type, the ratios  $f_i/f_k$  are measurable in each of the two solutions.

If we consider an electrolyte yielding  $q_+$  cations  $R$  of valency  $z_+$  and  $q_-$  anions  $X$  of valency  $z_-$ , and apply formula (658) both to the cations and to the anions, and eliminate  $\psi^\beta - \psi^\alpha$ , we obtain

$$\frac{(N_R^\beta)^{q_+} \cdot (N_X^\beta)^{q_-} \cdot (f_\pm^\beta)^{q_+ + q_-}}{(N_R^\alpha)^{q_+} \cdot (N_X^\alpha)^{q_-} \cdot (f_\pm^\alpha)^{q_+ + q_-}} = \left( \frac{N_0^\beta}{N_0^\alpha} \cdot \frac{f_0^\beta}{f_0^\alpha} \right)^r, \quad (661.1)$$

where  $r$  is defined by

$$r = \frac{q_+[V_R] + q_-[V_X]}{[V_0]}. \quad (661.2)$$

The exact formulæ (660) and (661) for membrane equilibria are due to Donnan and Guggenheim.

For the special case of ideal solutions, the conditions of membrane equilibrium become :  
for the solvent species

$$(P^\alpha - P^\beta)[V_0] = RT \log \frac{N_0^\beta}{N_0^\alpha}, \quad (662)$$

for the ionic species  $i$

$$(P^\alpha - P^\beta)[V_i] = RT \log \frac{N_i^\beta}{N_i^\alpha} + z_i \mathcal{F}(\psi^\beta - \psi^\alpha), \quad (663)$$

for two ionic species  $i$  and  $k$  of the same electric type

$$(P^\alpha - P^\beta)([V_i] - [V_k]) = RT \log \frac{N_i^\beta N_k^\alpha}{N_k^\beta N_i^\alpha}, \quad (664)$$

for an electrolyte yielding  $q_+$  cations  $R$  and  $q_-$  anions  $X$

$$(P^\alpha - P^\beta)(q_+[V_R] + q_-[V_X]) = RT \log \frac{(N_R^\beta)^{q_+} \cdot (N_X^\beta)^{q_-}}{(N_R^\alpha)^{q_+} \cdot (N_X^\alpha)^{q_-}}. \quad (665)$$

We see, according to (661.1) and (663), that whether the solutions be ideal or not, the conditions for membrane equilibria between the solute electrolytes are more complicated than those, (649) and (648), holding for a membrane impermeable to the solvent. If, however, the solutions are extremely dilute, in the sense that the mole fractions of all the solute species  $N_i$  are very small compared with unity and the mole fraction  $N_0$  of the solvent is very near unity, the value of  $P^\alpha - P^\beta$  will be at most of

the order of magnitude  $RT \frac{\sum_i N_i}{N_0 V_0}$ . Hence, the value of  $V_0(P^\alpha - P^\beta)$  will be at the most of the order of magnitude  $RT \sum_i N_i$ , and so negligible compared with  $RT$ . In this case, the term in  $P^\alpha - P^\beta$  occurring in formulæ (658), (663) may be neglected, and we then obtain the approximate formulæ (649), (648), which are exact for a membrane impermeable to the solvent.

**Contact Equilibrium.**—The most important case of non-osmotic membrane equilibrium is that of two phases with one

common component ion, the surface of separation being in effect a membrane permeable to the common ion but impermeable to all others. This may be referred to as "contact equilibrium". For example, for two metals, say Zn and Cu, in contact, there is equilibrium between the two phases as regards electrons  $\epsilon^-$ , but not as regards the positive ions  $\text{Zn}^{++}$  or  $\text{Cu}^{++}$ . The equilibrium is completely defined by

$$\mu_{\epsilon^-}^{\text{Zn}} = \mu_{\epsilon^-}^{\text{Cu}}, \quad (666)$$

the suffix  $\epsilon^-$  denoting, as usual, the component, and the index Zn or Cu the phase. Similarly, for a metallic electrode  $\alpha$ , of say Cu, dipping into a solution  $\beta$  containing ions of this metal, in this case  $\text{Cu}^{++}$ , the contact equilibrium is completely defined by

$$\bar{\mu}_{\text{Cu}^{++}}^{\beta} = \bar{\mu}_{\text{Cu}^{++}}^{\alpha}, \quad (667)$$

the electrode and solution being in equilibrium as regards the metallic ions only. In neither of these cases of contact equilibrium is any "contact electric potential difference" thermodynamically definable.

*Purely Chemical Cell.*—Consider the system composed of the following phases and membranes arranged in order, each phase being separated by partially permeable membranes from its neighbouring phases, and completely separated from the remaining phases.

Phase  $\alpha$ .—Containing inter alia species  $A$  and  $B$ .

Membrane I.—Permeable to  $B$  only.

Phase  $\beta$ .—Containing inter alia species  $B$  and  $C$ .

Membrane II.—Permeable to  $C$  only.

Phase  $\gamma$ .—Containing inter alia species  $C$  and  $A$ .

If the species  $A$ ,  $B$ ,  $C$  are all electrically neutral, then the two membrane equilibria are determined completely by the conditions

$$\mu_B^{\beta} = \mu_B^{\alpha}, \quad (668.1)$$

$$\mu_C^{\gamma} = \mu_C^{\beta}, \quad (668.2)$$

but in general

$$\mu_A^{\gamma} \neq \mu_A^{\alpha}, \quad (669)$$

that is to say, the phases  $\alpha$  and  $\gamma$  are not in equilibrium as regards the species  $A$ . If the phases  $\alpha$  and  $\gamma$  be now brought into contact through a membrane permeable to  $A$  only, there will be a flow of  $A$  from the one to the other in a direction determined by the

sign of  $(\mu_A^\gamma - \mu_A^\alpha)$ . This flow will of course upset the other membrane equilibria, which will readjust themselves. The flow of  $A$  through the auxiliary membrane and the accompanying readjustments will not cease until either the phases  $\alpha$  and  $\gamma$  are again separated, or the conditions

$$\mu_B^\beta = \mu_B^\alpha, \quad (669.1)$$

$$\mu_C^\gamma = \mu_C^\beta, \quad (669.2)$$

$$\mu_A^\alpha = \mu_A^\gamma, \quad (669.3)$$

are satisfied simultaneously.

We may call the system just described a “(purely) chemical cell,” the difference

$$\mu_A^\gamma - \mu_A^\alpha \quad (670)$$

the “chemico-motive force” of the cell for the component  $A$ . Bringing the phases  $\alpha$  and  $\gamma$  into contact through a membrane permeable only to  $A$ , we may call “closing the circuit” of the cell and separating these phases “breaking the circuit”. When the conditions (669) are satisfied simultaneously, we may say that the cell is “run down”.

More complicated (purely) chemical cells might be described containing a larger number of phases, membranes and components, but the general nature of any such cell, and the conditions of equilibrium will be similar to that of the above simple example.

The (purely) chemical cell is not of practical importance and, possibly for this reason, is not described or discussed in any text-books. We have described it here, as a clear understanding of a (purely) chemical cell should facilitate a complete comprehension of the nature of an “electro-chemical cell,” which we shall discuss next. We wish especially to emphasise that from a theoretical thermodynamic point of view, the electric charges of the ions is rather incidental, the fundamental factor at the base of any cell, whether purely chemical or electro-chemical, being the membrane or contact equilibria between successive phases.

*Electro-Chemical Cells.*—The only essential difference between an electro-chemical cell and a (purely) chemical cell is that in the former the membrane equilibria involve charged ions. Let us consider the following system, somewhat similar to the (purely) chemical cell discussed above, in which, however, the various species concerned are ions.

Phase  $\alpha$ .—Containing ions  $A$  and  $E$ .

Membrane I.—Permeable to ions  $E$  only.

Phase  $\beta$ .—Containing ions  $B$  and  $E$ .

Membrane II.—Permeable to ions  $B$  only.

Phase  $\gamma$ .—Containing ions  $A$  and  $B$ .

Membrane III.—Permeable to ions  $A$  only.

Phase  $\alpha'$ .—Chemically identical with phase  $\alpha$ .

The three membrane equilibria are defined completely by the conditions

$$\bar{\mu}_E^\beta = \bar{\mu}_E^\alpha, \quad (671.1)$$

$$\bar{\mu}_B^\gamma = \bar{\mu}_B^\beta, \quad (671.2)$$

$$\bar{\mu}_A^{\alpha'} = \bar{\mu}_A^\gamma, \quad (671.3)$$

but in general,

$$\bar{\mu}_E^\alpha \neq \bar{\mu}_E^{\alpha'}. \quad (672)$$

As compared with the example of a (purely) chemical cell, we have included in the present system one extra phase and membrane in order that the two extreme phases ("terminals")  $\alpha$  and  $\alpha'$  should have the same chemical composition. We may therefore write

$$\bar{\mu}_E^{\alpha'} - \bar{\mu}_E^\alpha = Z_E \mathcal{F}(\psi^{\alpha'} - \psi^\alpha), \quad (673)$$

and the difference of electric potential ( $\psi^{\alpha'} - \psi^\alpha$ ) thus defined is called the "electromotive force"  $\mathcal{E}$  of the cell. Putting the two phases  $\alpha$  and  $\alpha'$  into contact is called "closing the circuit," and separating them "breaking the circuit". On closing the circuit there will be an adjustment of membrane equilibria with net flow of electric charge round the circuit in a direction determined by the sign of  $\mathcal{E}$ . This will cease when the conditions

$$\bar{\mu}_E^\beta = \bar{\mu}_E^\alpha, \quad (674.1)$$

$$\bar{\mu}_B^\gamma = \bar{\mu}_B^\beta, \quad (674.2)$$

$$\bar{\mu}_A^{\alpha'} = \bar{\mu}_A^\gamma, \quad (674.3)$$

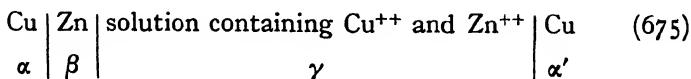
$$\bar{\mu}_E^{\alpha'} = \bar{\mu}_E^\alpha, \quad (674.4)$$

are satisfied simultaneously, and  $\mathcal{E}$  is zero, when the cell is said to be "run down".

We will now give a concrete example. We suppose the ionic species  $A$  to be  $\text{Cu}^{++}$ ,  $B$  to be  $\text{Zn}^{++}$ , and  $E$  to be electrons  $e^-$ . We also suppose the boundaries between the phases to form



natural membranes, each permeable to only one ionic species. We may thus obtain the cell



In the metallic phases we have the purely chemical homogeneous equilibrium conditions,

$$\bar{\mu}_{\text{Cu}^{++}}^{\alpha} + 2\bar{\mu}_{e^{-}}^{\alpha} = \bar{\mu}_{\text{Cu}^{++}}^{\alpha'} + 2\bar{\mu}_{e^{-}}^{\alpha'} = \mu_{\text{Cu}}^{\text{Cu}}, \quad (676.1)$$

$$\bar{\mu}_{\text{Zn}^{++}}^{\beta} + 2\bar{\mu}_{e^{-}}^{\beta} = \mu_{\text{Zn}}^{\text{Zn}}, \quad (676.2)$$

where  $\mu_{\text{Cu}}^{\text{Cu}}$  and  $\mu_{\text{Zn}}^{\text{Zn}}$  are independent of the electric states of the respective phases Cu and Zn. The contact equilibrium conditions are

$$\bar{\mu}_{e^{-}}^{\beta} = \bar{\mu}_{e^{-}}^{\alpha}, \quad (677.1)$$

$$\bar{\mu}_{\text{Zn}^{++}}^{\gamma} = \bar{\mu}_{\text{Zn}^{++}}^{\beta}, \quad (677.2)$$

$$\bar{\mu}_{\text{Cu}^{++}}^{\alpha'} = \bar{\mu}_{\text{Cu}^{++}}^{\alpha}. \quad (677.3)$$

Combining (673), (676), (677), we obtain for the electromotive force  $\mathcal{E}$

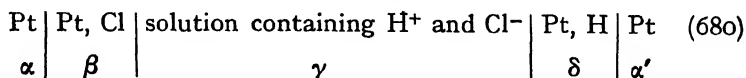
$$\begin{aligned} 2\mathcal{F}\mathcal{E} &= 2\mathcal{F}(\psi^{\alpha'} - \psi^{\alpha}) \\ &= -2\bar{\mu}_{e^{-}}^{\alpha'} + 2\bar{\mu}_{e^{-}}^{\alpha} \\ &= -\mu_{\text{Cu}}^{\text{Cu}} + \bar{\mu}_{\text{Cu}^{++}}^{\gamma} + \mu_{\text{Zn}}^{\text{Zn}} - \bar{\mu}_{\text{Zn}^{++}}^{\gamma}, \end{aligned} \quad (678)$$

or in terms of activity coefficients,

$$\mathcal{E} = \mathcal{E}^{\circ} + \frac{RT}{2\mathcal{F}} \log \left[ \frac{N_{\text{Cu}^{++}} \cdot f_{\text{Cu}^{++}}}{N_{\text{Zn}^{++}} \cdot f_{\text{Zn}^{++}}} \right]^{\gamma}, \quad (679)$$

where  $\mathcal{E}^{\circ}$  is independent of the composition of the phase  $\gamma$ .

As another example, we may take the cell



where the phases  $\beta$  and  $\delta$  refer to films at the surface of the platinum.

The conditions of homogeneous equilibrium are

$$\bar{\mu}_{\text{Cl}^{-}}^{\beta} - \bar{\mu}_{e^{-}}^{\beta} = \mu_{\text{Cl}}^{\beta}, \quad (681.1)$$

$$\bar{\mu}_{\text{H}^{+}}^{\delta} + \bar{\mu}_{e^{-}}^{\delta} = \mu_{\text{H}}^{\delta}, \quad (681.2)$$

where  $\mu_{\text{Cl}}^{\beta}$ ,  $\mu_{\text{H}}^{\delta}$  are independent of the electrical states of the phases. The conditions of contact equilibrium are :

$$\bar{\mu}_{e-}^{\beta} = \bar{\mu}_{e-}^{\alpha}, \quad (682.1)$$

$$\bar{\mu}_{\text{Cl}-}^{\gamma} = \bar{\mu}_{\text{Cl}-}^{\beta}, \quad (682.2)$$

$$\bar{\mu}_{\text{H}+}^{\delta} = \bar{\mu}_{\text{H}+}, \quad (682.3)$$

$$\bar{\mu}_{e-}^{\alpha'} = \bar{\mu}_{e-}^{\delta}. \quad (682.4)$$

Combining (681) with (682) we find for the electromotive force  $\mathcal{E}$

$$\begin{aligned} \mathcal{F}\mathcal{E} &= \mathcal{F}(\psi^{\alpha'} - \psi^{\alpha}) \\ &= -(\bar{\mu}_{e-}^{\alpha'} - \bar{\mu}_{e-}^{\alpha}) \\ &= -\mu_{\text{H}}^{\delta} + \bar{\mu}_{\text{H}+}^{\gamma} - \mu_{\text{Cl}}^{\beta} + \bar{\mu}_{\text{Cl}-}^{\gamma}, \end{aligned}$$

or

$$\mathcal{E} = \mathcal{E}^{\circ} + \frac{RT}{\mathcal{F}} \log [N_{\text{H}+} \cdot N_{\text{Cl}-} \cdot (f_{\text{H}, \text{Cl}})^2], \quad (683)$$

where  $\mathcal{E}^{\circ}$  depends on the state of the gases at the electrode surfaces, but is independent of the composition of the phase  $\gamma$ , and  $f_{\text{H}, \text{Cl}}$  is the mean activity coefficient  $f_{\pm}$  for HCl.

*Electromotive Force.*—The general case of an electro-chemical cell may be summarised as follows. We assume the two extreme phases to be of the same metal, and call these the “terminals” of the cell. The terminals are assumed not connected. We consider an infinitesimal process in which the only net transfer of charge is  $n$  Faradays from the left terminal  $\alpha$  to the right terminal  $\alpha'$ , the remaining change in the system being a purely chemical one. Let the increase in  $G$  corresponding to this purely chemical change be denoted by  $\Delta_{\text{ch}}G$ . Then the total increase  $\Delta G$  in  $G$  is given by

$$\Delta G = \Delta_{\text{ch}}G + n\mathcal{F}(\psi^{\alpha'} - \psi^{\alpha}), \quad (684)$$

which at equilibrium must, according to (51), be zero. Hence, for the electromotive force we have

$$\mathcal{E} = \psi^{\alpha'} - \psi^{\alpha} = -\frac{\Delta_{\text{ch}}G}{n\mathcal{F}}. \quad (685)$$

*Temperature Coefficient of Electromotive Force.*—By combining (685) with the Gibbs-Helmholtz relation (171), we obtain

immediately for the temperature coefficient of the electro-motive force,

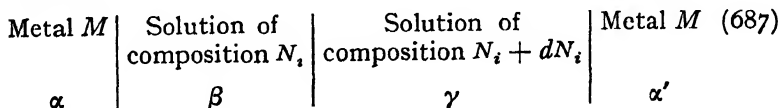
$$n\mathbf{F}\left(\frac{\partial \mathcal{E}/T}{\partial T}\right)_P = -\left(\frac{\partial \Delta_{\text{ch}}G/T}{\partial T}\right)_P = \frac{\Delta_{\text{ch}}H}{T^2}, \quad (686)$$

where  $\Delta_{\text{ch}}H$  is the heat of reaction of the chemical change corresponding to the passage of  $n$  Faradays from the one electrode to the other.

*Cells with Transference.*—The above treatment holds strictly for any cell in which no two liquid phases are in contact (unless in complete equilibrium with each other, in which case the inclusion or omission of one of them is immaterial). There is, however, a class of electro-chemical cells of practical importance which contain two solutions in the same solvent in direct contact. If there is a finite difference between the compositions of these solutions the passage of an infinitesimal current will not be a reversible process. If, for instance, the positive ion (cation)  $i$  is present in phase  $\alpha$ , but not in  $\beta$ , while the cation  $k$  is present in  $\beta$  but not in  $\alpha$ , then an infinitesimal passage of electric current in the one direction will transfer an infinitesimal quantity of the ion  $i$  from  $\alpha$  to  $\beta$ . Reversal of the current will, however, not return the ion  $i$  from  $\beta$  to  $\alpha$ , but will instead transfer the ion  $k$  from  $\beta$  to  $\alpha$ . If, however, the phases differ only infinitesimally in composition, this will not apply, and the passage of current will be reversible. It is true that simultaneously there is taking place an irreversible diffusion from one phase to the other, tending to equalise the compositions of the two phases.

The two processes diffusion and flow of current across the junction take place, however, at rates which vary according to different laws when the composition gradient across the boundary is altered. It seems reasonable to suppose that the two processes are merely superposed, and that the one may be ignored when considering the other.

For the sake of definiteness we shall consider as a special case the cell



and shall assume all the ions to be univalent. We shall use  $R^+$  to denote any positive ion (cation) and  $X^-$  to denote any negative ion (anion). The operators  $\sum_+$ ,  $\sum_-$  will denote respectively summation over all cations and over all anions. Suppose the circuit to

be open, and consider the infinitesimal reversible process at constant temperature and pressure in which one Faraday is transferred from the metal (electrode)  $\alpha$  to the metal (electrode)  $\alpha'$ . The process in detail consists of—

(a) the passage of one mole of  $R^+$  from the electrode  $\alpha$  to the solution  $\beta$ ;

(b) the passage of one mole of  $R^+$  from the solution  $\gamma$  to the electrode  $\alpha'$ ;

(c) the passage of  $t_R$  cations of each type  $R^+$  from  $\beta$  to  $\gamma$ ;

(d) the passage of  $t_X$  anions of each type  $X^-$  from  $\gamma$  to  $\beta$ .

The quantities  $t_R$ ,  $t_X$  are the "transport numbers" of the various ions. Their values will depend on the concentrations and mobilities of all the ions present. We have the identical relation between the transport numbers

$$\sum_+ t_R + \sum_- t_X = 1. \quad (688)$$

The equilibrium condition (with open circuit) is that for this process

$$\Delta G = 0, \quad (689)$$

or

$$(\bar{\mu}_{M^+}^\beta - \bar{\mu}_{M^+}^\alpha) + (\bar{\mu}_{M^+}^{\alpha'} - \bar{\mu}_{M^+}^\gamma) + \sum_+ t_R (\bar{\mu}_{R^+}^\gamma - \bar{\mu}_{R^+}^\beta) + \sum_- t_X (\bar{\mu}_{X^-}^\beta - \bar{\mu}_{X^-}^\gamma) = 0. \quad (690)$$

Using the operator  $d$  to denote the excess of a value in phase  $\gamma$  over the value in phase  $\beta$ , this becomes

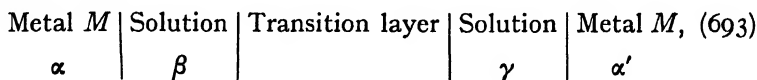
$$\begin{aligned} \mathcal{F}\mathcal{E} &= \bar{\mu}_{M^+}^{\alpha'} - \bar{\mu}_{M^+}^\alpha \\ &= d\bar{\mu}_{M^+} - \sum_+ t_R d\bar{\mu}_{R^+} + \sum_- t_X d\bar{\mu}_{X^-}, \end{aligned} \quad (691)$$

or using the identity (688)

$$\mathcal{F}\mathcal{E} = \sum_+ t_R d(\bar{\mu}_{M^+} - \bar{\mu}_{R^+}) + \sum_- t_X d(\bar{\mu}_{M^+} + \bar{\mu}_{X^-}). \quad (692)$$

This result is immediately extended to the case where the two solutions in contact with the electrodes ("electrode solutions") differ finitely in composition provided we assume that they are connected through a "transition layer" in which the composition varies continuously from that of the one electrode solution to that of the other. The manner in which the various concentrations, and so also the various transport numbers, will vary

along the transition layer will depend on the manner in which it is formed. This is not a thermodynamic question, and will not be discussed here. Assuming only that the variation of composition across the transition layer is continuous, we have for the cell,



by an obvious extension of (691)

$$\begin{aligned} \mathcal{F}\mathcal{E} &= \bar{\mu}_{M^+}^{\alpha'} - \bar{\mu}_{M^+}^{\alpha} \\ &= \bar{\mu}_{M^+}^{\gamma} - \bar{\mu}_{M^+}^{\beta} - \sum_{+}^{\gamma} t_{Rd} \bar{\mu}_{R^+} + \sum_{-}^{\gamma} t_{Xd} \bar{\mu}_{X^-}, \end{aligned} \quad (694)$$

where the integrals have to be evaluated for the range of composition corresponding to the transition layer.

If we now imagine the solutions to be ideal dilute (694) may, according to (625), be written

$$\mathcal{E} = \mathcal{E}_{E1} + \mathcal{E}_D, \quad (695)$$

where  $\mathcal{E}_{E1}$ , the "electrode potential," is defined by

$$\mathcal{F}\mathcal{E}_{E1} = RT \log \frac{N_{M^+}^{\gamma}}{N_{M^+}^{\beta}}, \quad (696)$$

and  $\mathcal{E}_D$ , the "diffusion potential," is defined by

$$\mathcal{F}\mathcal{E}_D = -RT \sum_{+}^{\gamma} t_{Rd} \log N_{R^+} + RT \sum_{-}^{\gamma} t_{Xd} \log N_{X^-}. \quad (697)$$

If, however, the solutions are not ideal dilute, (694) may be written

$$\mathcal{E} = \mathcal{E}_{E1} + \mathcal{E}_D + \mathcal{E}_S, \quad (698)$$

where  $\mathcal{E}_{E1}$  and  $\mathcal{E}_D$  are as defined by (696) and (697) respectively, while  $\mathcal{E}_S$  is defined by

$$\begin{aligned} \mathcal{F}\mathcal{E}_S &= RT \sum_R^{\gamma} t_{Rd} \log \frac{f_{M^+}}{f_{R^+}} + RT \sum_X^{\gamma} t_{Xd} \log f_{M^+} f_{X^-} \\ &= RT \sum_R^{\gamma} t_{Rd} \log \frac{(f_{M, X})^2}{(f_{R, X})^2} + RT \sum_X^{\gamma} t_{Xd} \log (f_{M, X})^2, \end{aligned} \quad (699)$$

where  $f_{R, X}$  denotes the mean activity coefficient of  $RX$ . As the expression "salt effect" is often used to refer to the devia-

tions from ideality of solutions of electrolytes,  $\mathcal{E}_S$  may be called the "salt effect potential". It is to be observed that (699) gives  $\mathcal{E}_S$  in terms of mean activity coefficients; a formula equivalent to this was first given by P. B. Taylor.

Any other cell with two different electrode solutions (cell with transference) may be treated similarly.

*Extremely Dilute Ionic Solutions.*—It is hardly necessary to mention that if the solutions in question are "extremely dilute" in the sense given in Chapter IX, the formulæ of the present chapter may be replaced by approximate formulæ in which the mole fraction  $N_i$  of each solute ion is replaced by its volume concentration  $C_i$ . In order to economise in space we shall give only a single example. In place of formula (683) we may, if the solution is extremely dilute, use the approximate formula

$$\mathcal{E} = \mathcal{E}^{\circ'} + \frac{RT}{\mathfrak{F}} \log [C_{H^+} C_{Cl^-} (f_{H^+}, Cl)^2], \quad (700)$$

where  $\mathcal{E}^{\circ'}$  is related to  $\mathcal{E}^{\circ}$  in (683) by

$$\mathcal{E}^{\circ'} = \mathcal{E}^{\circ} + \frac{2RT}{\mathfrak{F}} \log \frac{N_i}{C_i}, \quad (701.1)$$

or with sufficient accuracy by

$$\mathcal{E}^{\circ'} = \mathcal{E}^{\circ} + \frac{2RT}{\mathfrak{F}} \log V_0^{\circ}, \quad (701.2)$$

in which  $V_0^{\circ}$  means the molar volume of the pure solvent measured in litres per mole.  $\mathcal{E}^{\circ'}$ , defined by (700), is constant for the given solvent as long as the solutions are extremely dilute.

## NOTES AND REFERENCES

*Electrochemical Potentials.*—The electrochemical potentials were first defined by Guggenheim, *J. Phys. Chem.*, **33**, 842 (1929). The whole treatment of the present chapter is based on this article.

*Membrane Equilibrium.*—A review of membrane equilibria with full references to the literature is given by Donnan in *Rapport du troisième conseil de chimie*, Bruxelles (1928). The exact thermodynamic relations for membrane equilibria in solutions of the most general type have been derived by Donnan and Guggenheim in *Z. Physikal. Chem.*, A, **162**, 346 (1932).

*Purely Chemical Cells.*—The conception of a purely chemical cell is, so far as the author is aware, original. It is discussed in the author's contribution to the Willard Gibbs Commentary volume.

*Cells without Transference.*—The expression of the electromotive force of cells without transference in terms of activity coefficients is due to G. N. Lewis and is given in Lewis and Randall's "Thermodynamics".

*Cells with Transference.*—The correct general thermodynamic treatment of cells with transference is due to P. B. Taylor, *J. Phys. Chem.*, **31**, 1478 (1927).

The present treatment is based on an article by Guggenheim, *J. Phys. Chem.*, **34**, 1758 (1930). Detailed discussion of the nature of the transition layer and its dependence on the experimental procedure is given by Guggenheim, *J. Am. Chem. Soc.*, **52**, 1315 (1930). In this paper are explained the conditions under which the value of  $E_D$  is given by a formula due to Henderson in *Z. Physikal. Chem.*, **59**, 118 (1907), and the conditions under which its value is given by a formula due to Planck, *Wied. Ann.*, **39**, 161 (1890), and **40**, 561 (1890). Attempts to evaluate the integral  $E_D$  in two simple cases have been made by Unmack and Guggenheim, *Kgl. Dansk. Vid. Selsk., Mat-Fys. Medd.*, **10**, No. 8 (1930), and Guggenheim and Unmack, *Kgl. Dansk. Vid. Selsk., Mat-Fys. Medd.*, **10**, No. 14 (1931).

## CHAPTER XI

### GRAVITATIONAL FIELD

*Nature of Gravitational Field.*—The formulæ of Chapters I and II are easily extended so as to take account of the presence of a gravitational field. Such a field is characterised by a gravitational potential  $\phi$  with a definite value at each place. The modification of the gravitational field by the presence of matter in quantities of the order of magnitude of those dealt with in ordinary chemical and physical processes is completely negligible compared with the earth's field or any other field of comparable importance. We may therefore regard the gravitational field as completely independent of the state of the thermodynamic system considered. In this sense, we call the gravitational field an "external field," and regard the gravitational potential at each point as independent of the presence or state of any matter there. It is owing to this fact that, although the abstract theories of gravitational and electrostatic potential are in many ways parallel, yet their significance for thermodynamic systems is rather different.

*Phases in Gravitational Field.*—Since a phase was defined as completely homogeneous in its properties and *state*, two portions of matter of identical temperature and composition must be considered as different phases if they are differently situated with respect to a gravitational field. It follows that the mere presence of a gravitational field excludes the possibility of a phase of finite depth in the direction of the field. In the presence of a gravitational field even the simplest possible kind of system must be considered as composed of a continuous sequence of phases each differing infinitesimally from its neighbours.

*Thermodynamic Functions in Gravitational Field.*—The characteristic property of the gravitational potential  $\phi$  is that the work  $w$  required to bring a quantity of matter of mass  $M$  from a place where the potential is  $\phi^\alpha$  to a place where it is  $\phi^\beta$  is given by

$$w = M(\phi^\beta - \phi^\alpha), \quad (702)$$

thus depending on the mass but not on the chemical nature of the matter. If the molar mass ("molecular weight") of the



species  $i$  is denoted by  $M_i$  and the number of moles of this species transferred is  $\lambda_i$ , then (702) becomes

$$w = \sum_i \lambda_i M_i (\phi^\beta - \phi^\alpha). \quad (703)$$

In transferring  $dn_i$  moles of the species  $i$  from the phase  $\alpha$  to the phase  $\beta$ , the gravitational work is

$$(\phi^\beta - \phi^\alpha) M_i dn_i.$$

Thus the formula (20.0) for  $dE^\alpha$  must for each phase  $\alpha$  contain the extra terms  $\sum_i \phi^\alpha M_i dn_i$ . That is to say

$$dE^\alpha = T^\alpha dS^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha. \quad (704)$$

For the other characteristic functions  $H$ ,  $F$  and  $G$ , defined respectively by (21), (24) and (25), we have

$$dH^\alpha = T^\alpha dS^\alpha + V^\alpha dP^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha, \quad (705)$$

$$dF^\alpha = -S^\alpha dT^\alpha - P^\alpha dV^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha, \quad (706)$$

$$dG^\alpha = -S^\alpha dT^\alpha + V^\alpha dP^\alpha + \sum_i (\mu_i^\alpha + M_i \phi^\alpha) dn_i^\alpha. \quad (707)$$

It follows that to take account of the effect of a gravitational field one has merely to replace  $\mu_i^\alpha$  throughout by

$$(\mu_i^\alpha + M_i \phi^\alpha).$$

Although in all thermodynamic formulæ the quantity  $\phi^\alpha$  occurs only in combinations of the form  $(\mu_i^\alpha + M_i \phi^\alpha)$ , yet the gravitational potential difference  $\Delta\phi$  between two phases, in contrast to the electric potential difference  $\Delta\psi$ , is thermodynamically determinate, owing to the fact that its value is independent of the presence and nature of the phase there. The phase may therefore be removed without altering  $\phi^\alpha$  and then  $\phi^\alpha$  determined in empty space by direct mechanical measurements.

*Equilibrium in Gravitational Field.*—For the equilibrium as regards the species  $i$  between two phases  $\alpha$  and  $\beta$ , defined not merely by their temperature, pressure and composition, but also by their gravitational potentials, we have in analogy with (82) the general condition,

$$\mu_i^\alpha + M_i \phi^\alpha = \mu_i^\beta + M_i \phi^\beta. \quad (708)$$

*Single Component in Gravitational Field.*—For the gravita-

tional equilibrium of a single component we have, according to (708),

$$d\mu + Md\phi = 0. \quad (709)$$

But, according to (153), for constant temperature and composition,

$$d\mu = VdP. \quad (710)$$

Substituting from (710) into (709), we obtain

$$VdP = -Md\phi, \quad (711)$$

or, writing  $\rho$  for the density defined by

$$\rho = \frac{M}{V}, \quad (712)$$

we obtain

$$dP = -\rho d\phi, \quad (713)$$

in agreement with the general condition of hydrostatic equilibrium.

For the case of a perfect gas we have, according to (199),

$$V = \frac{RT}{P}. \quad (714)$$

Substituting (714) into (711), we obtain

$$RTd \log P = -Md\phi, \quad (715)$$

and integrating,

$$RT \log \frac{P^\beta}{P^\alpha} = M(\phi^\alpha - \phi^\beta). \quad (716)$$

For an incompressible liquid, on the other hand,  $V$  is independent of  $P$ , and (711) can be integrated directly to give

$$V(P^\beta - P^\alpha) = M(\phi^\alpha - \phi^\beta), \quad (717)$$

or, introducing the density  $\rho$  defined by (712),

$$P^\beta - P^\alpha = \rho(\phi^\alpha - \phi^\beta). \quad (718)$$

*Perfect Gases.*—For the equilibrium of perfect gases, whether single or in a mixture, in a gravitational field at constant temperature, we obtain, by substituting from (321) into (708),

$$RT \log \frac{p_i^\beta}{p_i^\alpha} = M_i(\phi^\alpha - \phi^\beta), \quad (719)$$

or in terms of volume concentrations  $C_i$ , using (326),

$$RT \log \frac{C_i^\beta}{C_i^\alpha} = M_i(\phi^\alpha - \phi^\beta). \quad (720)$$

The relation (720) may also be written in the form,

$$\frac{C_i^\beta}{C_i^\alpha} = \exp. \left\{ \frac{M_i(\phi^\alpha - \phi^\beta)}{RT} \right\} \quad (721)$$

which is Boltzmann's formula for a gravitational field. In the special case of a single gas (719) is identical with (716).

*Solution in Gravitational Field.*—For the gravitational equilibrium of a solution we have for each species, using the operator  $d$  to denote the difference in value for two contiguous layers, according to (708),

$$d(\mu_i + M_i\phi) = 0. \quad (722)$$

Using the shorthand notation introduced in Chapter V of the operator  $D$  to denote the difference in the value of a function due to variation of composition at constant temperature and constant pressure, we may, according to (153), write—

$$d\mu_i = D\mu_i + V_i dP. \quad (723)$$

Substituting (723) into (722), we obtain

$$D\mu_i + V_i dP + M_i d\phi = 0. \quad (724)$$

But, according to (33), we have

$$\sum_i N_i D\mu_i = 0. \quad (725)$$

Multiplying (724) by  $N_i$ , summing for all  $i$ , and using (725), we obtain

$$\sum_i N_i V_i dP + \sum_i N_i M_i d\phi = 0. \quad (726)$$

Introducing the mean molar volume  $V$  defined by,

$$V = \sum_i N_i V_i, \quad (727)$$

and the mean molar mass  $M$  defined by,

$$M = \sum_i N_i M_i, \quad (728)$$

(726) may be written,

$$V dP + M d\phi = 0, \quad (729)$$

which is formally the same as (711), the equation of hydrostatic equilibrium for a single component.

Substituting for  $dP$  from (729) into (724), we obtain,

$$D\mu_i + \left\{ M_i - V_i \frac{\sum_k N_k M_k}{\sum_k N_k V_k} \right\} d\phi = 0. \quad (730)$$

*Ideal Solution in Gravitational Field.*—For an ideal solution, according to (458),

$$D\mu_i = RT d \log N_i, \quad (731)$$

and (730) becomes,

$$RT d \log N_i + \left\{ M_i - V_i \frac{\sum_k N_k M_k}{\sum_k N_k V_k} \right\} d\phi = 0. \quad (732)$$

*Binary Ideal Solution.*—A direct integration of (732) is not generally possible, but is so in the special case of a binary solution, if its compressibility is neglected. Denoting the two components by  $A$  and  $B$ , (732) becomes,

$$\begin{aligned} -\frac{d\phi}{RT} &= \frac{dN_B}{N_B} \cdot \frac{N_A V_A + N_B V_B}{M_B(N_A V_A + N_B V_B) - V_B(N_A M_A + N_B M_B)} \\ &= \frac{dN_B}{N_B} \cdot \frac{N_A V_A + N_B V_B}{N_A(M_B V_A - M_A V_B)} \\ &= \frac{dN_B}{M_B V_A - M_A V_B} \left\{ \frac{V_A}{N_B} - \frac{V_B}{N_A} \right\}. \end{aligned} \quad (733)$$

Since by definition

$$N_A = 1 - N_B, \quad (734)$$

(733) may be written,

$$-\frac{d\phi}{RT} = \frac{dN_B}{M_B V_A - M_A V_B} \left\{ \frac{V_A}{N_B} - \frac{V_B}{1 - N_B} \right\}, \quad (735)$$

and direct integration gives,

$$-\left(M_B - M_A \frac{V_B}{V_A}\right) \cdot \frac{\phi^\beta - \phi^\alpha}{RT} = \log \frac{N_B^\beta}{N_B^\alpha} + \frac{V_B}{V_A} \log \frac{N_A^\beta}{N_A^\alpha}, \quad (736)$$

or

$$\exp. \left\{ \left(M_B - M_A \frac{V_B}{V_A}\right) \frac{\phi^\alpha - \phi^\beta}{RT} \right\} = \frac{N_B^\beta}{N_B^\alpha} \left( \frac{N_A^\beta}{N_A^\alpha} \right)^{\frac{V_B}{V_A}}. \quad (737)$$

If the solution is "extremely dilute" in the sense of Chapter IX, with respect to the component  $B$ , then the second factor on the right of (737) approaches unity, and (737) simplifies to

$$\frac{C_B^\beta}{C_B^\alpha} = \exp. \left\{ \left( M_B - M_A \frac{V_B}{V_A} \right) \frac{\phi^\alpha - \phi^\beta}{RT} \right\}, \quad (738)$$

the formula used by Perrin in his classical work on the distribution of colloidal particles in a gravitational field.

*Extremely Dilute Ideal Solution in Gravitational Field.*—As already mentioned (732) is not directly integrable, except in the case of a binary solution. If, however, the solution is "extremely dilute," in the sense of Chapter IX, as well as ideal, then (732) takes the approximate form,

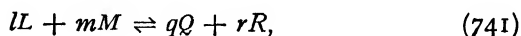
$$RT d \log N_i + \left\{ M_i - V_i \frac{M_0}{V_0} \right\} d\phi = 0. \quad (739)$$

Neglecting compressibility, this can be directly integrated, giving

$$\frac{N_i^\beta}{N_i^\alpha} = \frac{C_i^\beta}{C_i^\alpha} = \exp. \left\{ M_i - V_i \frac{M_0}{V_0} \right\} \frac{\phi^\alpha - \phi^\beta}{RT}. \quad (740)$$

Formula (738) obtained for an extremely dilute ideal binary solution is a special case of (740).

*Law of Mass Action in Gravitational Field.*—For the reaction,



the most general form for the law of mass action in the absence of a gravitational field is, according to (97),

$$q\mu_Q + r\mu_R - l\mu_L - m\mu_M = \text{constant}. \quad (742)$$

In the presence of a gravitational field the corresponding equilibrium condition is clearly

$$q(\mu_Q + M_Q\phi) + r(\mu_R + M_R\phi) - l(\mu_L + M_L\phi) - m(\mu_M + M_M\phi) = \text{constant}. \quad (743)$$

But, according to the law of conservation of mass, we have,

$$qM_Q + rM_R - lM_L - mM_M = 0. \quad (744)$$

Multiplying (744) by  $\phi$ , and subtracting from (743), we obtain (742). It follows that any chemical equilibrium is independent of the gravitational potential.

## NOTES AND REFERENCES

*Thermodynamics of Gravitational Field.*—The treatment of the present chapter is that of Gibbs, *vide* "Collected Works". A detailed discussion of dissociative equilibrium in a gravitational (or *external* electric field) is given by Milne in *Proc. Camb. Phil. Soc.*, **22**, 493 (1925). The treatment given by Lewis and Randall is ambiguous. Their function  $\bar{F}_i$ , which they call the "partial molar free energy," is incompletely defined. It is not the same as the chemical potential  $\mu_i$ , but is equal to the sum  $\mu_i + M_i\phi$ . Their formula (9) in Chapter XXI, corresponding to our formula (730), is incorrect.

*Binary Ideal Solution.*—The formula given for the gravitational equilibrium of binary ideal solutions, other than extremely dilute ones, is, so far as the author is aware, new.

## CHAPTER XII

### SURFACE PHASES

*Surface Phases.*—Suppose two phases,  $\alpha$  and  $\beta$ , to be in contact. The boundary between the two phases will not be a sharply defined geometrical surface, but rather a thin film across which the physical properties vary from those of the interior of the one phase to those of the interior of the other phase. Thus, in Fig. 7 we may suppose the nature of the phase  $\alpha$  to remain completely homogeneous as far as the geometrical surface  $AA'$ , while that of the phase  $\beta$  remains completely homogeneous as far as the geometrical surface  $BB'$ . The matter contained in the film between  $AA'$  and  $BB'$  is not homogeneous, but has properties varying continuously from those of the interior of  $\alpha$  at the surface  $AA'$  to those of the interior of  $\beta$  at the surface  $BB'$ .

There is a certain degree of arbitrariness in the exact positions assigned to the surfaces  $AA'$  and  $BB'$ , and so to the thickness of the film. It will, however, always be possible to assign positions to  $AA'$  and  $BB'$  such that the thickness of the film corresponds to only a few molecules. The thickness of the film is then negligibly

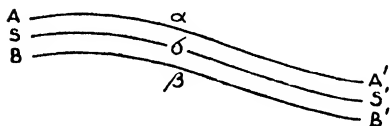


FIG. 7.

small compared with the radii of curvature of the surfaces  $AA'$  and  $BB'$ . We may therefore assume the two surfaces  $AA'$  and  $BB'$  to be of practically identical size and shape, and the normal distance between them (the thickness of the film) to be constant.

For the thermodynamic treatment of the film it is convenient to choose a geometrical surface  $SS'$  of the same size and shape as  $AA'$  and  $BB'$ , and lying between them. Since each phase  $\alpha$  and  $\beta$  is homogeneous, the film separating them will also be homogeneous along directions tangential to the surface  $SS'$ , though not in directions normal thereto. In this sense we may call the film a "surface phase". A surface phase will be denoted by the letter  $\sigma$ .

*Extent of Surface Phase.*—The thickness of the given surface phase being the same throughout, its extent is conveniently measured by the area of the surface  $\sigma$ . This is called the area of the surface phase  $\sigma$ , and will be denoted by  $A^\sigma$ . The value of  $A^\sigma$  is clearly independent of the exact choice of the position of the surface  $\sigma$  as long as it lies between  $AA'$  and  $BB'$ .

*Composition of Surface Phase and Surface Concentrations.*—The composition of the surface phase  $\sigma$  separating the homogeneous phases  $\alpha$  and  $\beta$  is conveniently defined by the quantities  $n_i^\sigma$  representing the number of moles of the species  $i$  in the surface film in excess of the number computed on the assumption that the phases  $\alpha$  and  $\beta$  both remained homogeneous right up to the surface  $SS'$ . According to this definition, it is possible for some of the  $n_i^\sigma$  to have negative values. The values of the  $n_i^\sigma$  will depend on the exact position assigned to the surface  $SS'$ .

The quantities  $n_i^\sigma$  are, of course, extensive quantities, their values being proportional to the extent of the surface phase. For describing the nature of the film, independently of its extent, it is convenient to define intensive quantities  $\Gamma_i^\sigma$  called "surface concentrations" by the relation

$$\Gamma_i^\sigma = \frac{n_i^\sigma}{A^\sigma}. \quad (745)$$

The surface concentrations  $\Gamma_i^\sigma$  of some species, like the quantities  $n_i^\sigma$ , may be negative. And also the values of the  $\Gamma_i^\sigma$  will depend on the exact position assigned to the geometrical surface.

If we select some one chemical species denoted by the suffix 0, whose volume concentrations in the two phases  $\alpha$  and  $\beta$  are not identical, then it is always possible to choose the exact position of the geometrical surface  $SS'$  in such a way that the total number of moles of the species 0 in the whole system is exactly equal to what it would be if the phases  $\alpha$  and  $\beta$  both remained homogeneous right up to the surface  $SS'$ . With this choice of the surface  $SS'$ , we have

$$n_0^\sigma = 0, \quad (746)$$

$$\Gamma_0^\sigma = 0. \quad (747)$$

The values of  $n_i^\sigma$  for all the chemical species  $i$  other than the species 0 are often referred to as the number of moles of the respective species  $i$  "adsorbed" at the surface  $\sigma$ . The corresponding values of  $\Gamma_i^\sigma$  may be called the "concentrations adsorbed" of the various species  $i$  at the surface  $\sigma$ . The quantities and concentrations adsorbed may thus be either positive or negative.



*Surface Energy.*—The energy  $E^\sigma$  of the surface phase  $\sigma$  is defined as the excess of the energy of the whole system (phase  $\alpha$  + phase  $\beta$  + surface film) over its value for the two phases,  $\alpha$  and  $\beta$ , computed on the assumption that each of them remained homogeneous right up to the surface  $SS'$ .

Thus, in a system of several homogeneous phases  $\alpha$  and several surface phases  $\sigma$ , having assigned exact positions to the hypothetical geometrical surfaces separating the various pairs of homogeneous phases, we compute the energy  $E^\alpha$  of each homogeneous phase  $\alpha$  on the supposition that it remained homogeneous right up to the chosen geometrical surfaces. The energy  $E$  of the whole system is then of the form

$$E = \sum_{\alpha} E^{\alpha} + \sum_{\sigma} E^{\sigma}, \quad (748)$$

where corresponding to each surface phase  $\sigma$  is a surface energy  $E^\sigma$ .

*Surface Entropy.*—The definition of the entropy  $S^\sigma$  of the surface phase  $\sigma$  is exactly analogous to that of the surface energy  $E^\sigma$ . We imagine the entropy  $S^\alpha$  of each homogeneous phase  $\alpha$  computed on the supposition that the phase remained homogeneous right up to the fictitious geometrical bounding surface. The total entropy  $S$  of the system is of the form

$$S = \sum_{\alpha} S^{\alpha} + \sum_{\sigma} S^{\sigma}, \quad (749)$$

where there is a surface entropy  $S^\sigma$  corresponding to each surface.

*Surface Tension.*—The only mechanical work that can be done on or by a surface phase  $\sigma$  is that corresponding to a change of the surface area  $A^\sigma$ . The work  $w$  required to be done to increase the surface area  $A^\sigma$  of the surface phase  $\sigma$  by an infinitesimal amount of  $dA^\sigma$ , without any appreciable change in the homogeneous phases is given by

$$w = \gamma dA^\sigma, \quad (750)$$

where  $\gamma$  is the "surface tension" of the surface  $\sigma$ . Comparison of (750) with (17) shows the analogy on the one hand between  $V^\alpha$  in a homogeneous phase  $\alpha$  and  $A^\sigma$  in a surface phase  $\sigma$  and on the other between  $P^\alpha$  in a homogeneous phase  $\alpha$  and  $-\gamma^\sigma$  in a surface phase  $\sigma$ .

*Relation between Surface Energy, Surface Area and Surface Composition.*—A surface phase of given area  $A^\sigma$  and composition, defined by the  $n_i^\sigma$  can still undergo variations by the absorption or emission of heat. Therefore to fix its state completely we require one other independent variable which we may take to be

the surface entropy  $S^\sigma$ . We can then, by an argument analogous to that used to deduce (20.0), obtain the formula

$$dE^\sigma = T^\sigma dS^\sigma + \gamma^\sigma dA^\sigma + \sum_i \mu_i^\sigma dn_i^\sigma, \quad (751)$$

where  $\mu_i^\sigma$  is called the chemical potential of the species  $i$  in the surface phase  $\sigma$ .

*Characteristic Functions.*—In a system of several homogeneous phases  $\alpha$  and surface phases  $\sigma$ , if we choose as independent variables the quantities  $S^\alpha$ ,  $S^\sigma$ ,  $V^\alpha$ ,  $A^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is the total energy  $E$ . Its variation is expressed in terms of those of the independent variables by

$$\begin{aligned} dE = & \sum_\alpha T^\alpha dS^\alpha - \sum_\alpha P^\alpha dV^\alpha + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha \\ & + \sum_\sigma T^\sigma dS^\sigma + \sum_\sigma \gamma^\sigma dA^\sigma + \sum_\sigma \sum_i \mu_i^\sigma dn_i^\sigma. \end{aligned} \quad (752)$$

In any change in which the volume  $V^\alpha$  of every homogeneous phase  $\alpha$  is kept constant, and the surface area  $A^\sigma$  of every surface phase  $\sigma$  is kept constant, the work  $w$  done on the system will be zero and the heat absorbed  $q$  will be equal to the increase  $\Delta E$  in  $E$ .

If we choose as independent variables the quantities  $S^\alpha$ ,  $S^\sigma$ ,  $P^\alpha$ ,  $A^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is the quantity  $H$  defined by

$$\begin{aligned} H &= E + \sum_\alpha P^\alpha V^\alpha \\ &= \sum_\alpha E^\alpha + \sum_\alpha P^\alpha V^\alpha + \sum_\sigma E^\sigma. \end{aligned} \quad (753)$$

Its variation is expressed in terms of those of the independent variables by

$$\begin{aligned} dH &= \sum_\alpha T^\alpha dS^\alpha + \sum_\alpha V^\alpha dP^\alpha + \sum_\alpha \sum_i \mu_i^\alpha dn_i^\alpha \\ &+ \sum_\sigma T^\sigma dS^\sigma + \sum_\sigma \gamma^\sigma dA^\sigma + \sum_\sigma \sum_i \mu_i^\sigma dn_i^\sigma. \end{aligned} \quad (754)$$

In any change in which the pressure  $P^\alpha$  of every homogeneous phase  $\alpha$  is kept constant and the surface area  $A^\sigma$  of every surface phase  $\sigma$  is kept constant, the work  $w$  done on the system will be  $-\Delta \sum_\alpha P^\alpha V^\alpha$ , and so the heat  $q$  absorbed will be given by

$$\begin{aligned} q &= \Delta E + \sum_\alpha \Delta(P^\alpha V^\alpha), \\ &= \Delta H. \end{aligned}$$

If we choose as independent variables the quantities  $S^\alpha$ ,  $S^\sigma$ ,  $V^\alpha$ ,  $\gamma^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is  $\bar{E}$  defined by

$$\begin{aligned}\bar{E} &= E - \sum_{\sigma} \gamma^\sigma A^\sigma \\ &= \sum_{\alpha} E^\alpha + \sum_{\sigma} E^\sigma - \sum_{\sigma} \gamma^\sigma A^\sigma,\end{aligned}\quad (755)$$

and its variation is expressed in terms of those of the independent variables by

$$\begin{aligned}d\bar{E} &= \sum_{\alpha} T^\alpha dS^\alpha - \sum_{\alpha} P^\alpha dV^\alpha + \sum_{\alpha} \sum_i \mu_i^\alpha dn_i^\alpha \\ &+ \sum_{\sigma} T^\sigma dS^\sigma - \sum_{\sigma} A^\sigma d\gamma^\sigma + \sum_{\sigma} \sum_i \mu_i^\sigma dn_i^\sigma.\end{aligned}\quad (756)$$

In any change in which the volumes  $V^\alpha$  of the homogeneous phases and the surface tensions  $\gamma^\sigma$  of the surface phases are kept constant, the work  $w$  done on the system is  $\Delta \sum_{\sigma} \gamma^\sigma A^\sigma$ , and so the heat  $q$  absorbed by the system is given by

$$\begin{aligned}q &= \Delta E - \Delta \sum_{\sigma} \gamma^\sigma A^\sigma \\ &= \Delta \bar{E}.\end{aligned}\quad (757)$$

If the independent variables are chosen to be  $S^\alpha$ ,  $S^\sigma$ ,  $P^\alpha$ ,  $\gamma^\alpha$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is  $\bar{H}$  defined by

$$\bar{H} = E + \sum_{\alpha} P^\alpha V^\alpha - \sum_{\sigma} \gamma^\sigma A^\sigma, \quad (758)$$

and its variation is expressed in terms of those of the independent variables by

$$\begin{aligned}d\bar{H} &= \sum_{\alpha} T^\alpha dS^\alpha + \sum_{\alpha} V^\alpha dP^\alpha + \sum_{\alpha} \sum_i \mu_i^\alpha dn_i^\alpha \\ &+ \sum_{\alpha} T^\alpha dS^\alpha - \sum_{\sigma} A^\sigma d\gamma^\sigma + \sum_{\sigma} \sum_i \mu_i^\sigma dn_i^\sigma.\end{aligned}\quad (759)$$

For any change taking place in which the pressure  $P^\alpha$  of each homogeneous phase and the surface tension  $\gamma^\sigma$  of each surface phase are kept constant, the work  $w$  done on the system is given by

$$w = - \Delta \sum_{\alpha} P^\alpha V^\alpha + \Delta \sum_{\sigma} \gamma^\sigma A^\sigma, \quad (760)$$

and so the heat  $q$  absorbed by the system is given by

$$\begin{aligned}q &= \Delta E + \Delta \sum_{\alpha} P^\alpha V^\alpha - \Delta \sum_{\sigma} \gamma^\sigma A^\sigma \\ &= \Delta \bar{H}.\end{aligned}\quad (761)$$

If, on the other hand, we choose as independent variables the quantities  $T^\alpha$ ,  $T^\sigma$ ,  $V^\alpha$ ,  $A^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is the Helmholtz free energy  $F$  defined by

$$F = E - \sum_{\alpha} T^{\alpha} S^{\alpha} - \sum_{\sigma} T^{\sigma} S^{\sigma}, \quad (762)$$

and its variation in terms of the independent variables is given by

$$\begin{aligned} dF = & - \sum_{\alpha} S^{\alpha} dT^{\alpha} - \sum_{\alpha} P^{\alpha} dV^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\ & - \sum_{\sigma} S^{\sigma} dT^{\sigma} + \sum_{\sigma} \gamma^{\sigma} dA^{\sigma} + \sum_{\sigma} \sum_i \mu_i^{\sigma} dn_i^{\sigma}. \end{aligned} \quad (763)$$

If we choose as independent variables the quantities  $T^\alpha$ ,  $T^\sigma$ ,  $P^\alpha$ ,  $A^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is  $G$  defined by

$$G = F + \sum_{\alpha} P^{\alpha} V^{\alpha}, \quad (764)$$

and its variation in terms of those of the independent variables is given by

$$\begin{aligned} dG = & - \sum_{\alpha} S^{\alpha} dT^{\alpha} + \sum_{\alpha} V^{\alpha} dP^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\ & - \sum_{\sigma} S^{\sigma} dT^{\sigma} + \sum_{\sigma} \gamma^{\sigma} dA^{\sigma} + \sum_{\sigma} \sum_i \mu_i^{\sigma} dn_i^{\sigma}. \end{aligned} \quad (765)$$

If as independent variables we choose  $T^\alpha$ ,  $T^\sigma$ ,  $V^\alpha$ ,  $\gamma^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is  $\bar{F}$  defined by

$$\bar{F} = F - \sum_{\sigma} \gamma^{\sigma} A^{\sigma}, \quad (766)$$

and its variation is expressed in terms of those of the independent variables by

$$\begin{aligned} d\bar{F} = & - \sum_{\alpha} S^{\alpha} dT^{\alpha} - \sum_{\alpha} P^{\alpha} dV^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\ & - \sum_{\sigma} S^{\sigma} dT^{\sigma} - \sum_{\sigma} A^{\sigma} d\gamma^{\sigma} + \sum_{\sigma} \sum_i \mu_i^{\sigma} dn_i^{\sigma}. \end{aligned} \quad (767)$$

Finally, if we choose as independent variables  $T^\alpha$ ,  $T^\sigma$ ,  $P^\alpha$ ,  $\gamma^\sigma$ ,  $n_i^\alpha$ ,  $n_i^\sigma$ , the characteristic function is  $\bar{G}$ , defined by

$$\bar{G} = F + \sum_{\alpha} P^{\alpha} V^{\alpha} - \sum_{\sigma} \gamma^{\sigma} A^{\sigma}, \quad (768)$$

and its variation in terms of those of the independent variables is given by

$$\begin{aligned} d\bar{G} = & - \sum_{\alpha} S^{\alpha} dT^{\alpha} + \sum_{\alpha} V^{\alpha} dP^{\alpha} + \sum_{\alpha} \sum_i \mu_i^{\alpha} dn_i^{\alpha} \\ & - \sum_{\sigma} S^{\sigma} dT^{\sigma} - \sum_{\sigma} A^{\sigma} d\gamma^{\sigma} + \sum_{\sigma} \sum_i \mu_i^{\sigma} dn_i^{\sigma}. \end{aligned} \quad (769)$$

It is worth noticing that by the inclusion of surface phases in the thermodynamic system the number of kinds of characteristic function is doubled. The cause of this is that we may choose as the new independent variables either the surface areas  $A^\sigma$  or the surface tensions  $\gamma^\sigma$ .

*Analogue of Gibbs-Duhem Relation.*—All the differential relations (752), (754), (756), (759), (763), (765), (767), (769) are homogeneous, and of first degree in all the capacity factors, and so are directly integrable, keeping all the intensity factors  $T^\alpha$ ,  $T^\sigma$ ,  $P^\alpha$ ,  $\gamma^\sigma$ ,  $\mu_i^\alpha$ ,  $\mu_i^\sigma$  constant. Whichever of these equations we integrate, the result is the same, namely

$$\bar{G} = \sum_{\alpha} n_i^\alpha \mu_i^\alpha + \sum_{\sigma} n_i^\sigma \mu_i^\sigma. \quad (770)$$

Differentiating (770) we obtain

$$d\bar{G} = \sum_{\alpha} n_i^\alpha d\mu_i^\alpha + \sum_{\alpha} \mu_i^\alpha dn_i^\alpha + \sum_{\sigma} n_i^\sigma d\mu_i^\sigma + \sum_{\sigma} \mu_i^\sigma dn_i^\sigma. \quad (771)$$

Comparing (771) with (769) we obtain

$$\begin{aligned} - \sum_{\alpha} S^\alpha dT^\alpha + \sum_{\alpha} V^\alpha dP^\alpha - \sum_{\alpha} n_i^\alpha d\mu_i^\alpha \\ - \sum_{\sigma} S^\sigma dT^\sigma - \sum_{\sigma} A^\sigma d\gamma^\sigma - \sum_{\sigma} n_i^\sigma d\mu_i^\sigma = 0. \end{aligned} \quad (772)$$

Confining our attention to variations of only one surface phase  $\sigma$ , the internal equilibrium of all the homogeneous phases  $\alpha$  being preserved, (772) simplifies to

$$- S^\sigma dT^\sigma - A^\sigma d\gamma^\sigma - \sum_i n_i^\sigma d\mu_i^\sigma = 0. \quad (773)$$

In the special case of a variation at constant temperature (773) becomes

$$dT^\sigma = 0 \quad - A^\sigma d\gamma^\sigma - \sum_i n_i^\sigma d\mu_i^\sigma = 0, \quad (774)$$

the analogue of the Gibbs-Duhem relation (33).

*Adiabatic Processes.*—Exactly as in the absence of surface effects we have for an adiabatic change for the heat absorbed and the work  $w$  done on a system at uniform temperature

$$q = 0, \quad (775.1)$$

$$w = dE, \quad (775.2)$$

and, so, according to (5) and (6), we have for the entropy change:

For a natural process,

$$\sum_{\alpha} dS^\alpha + \sum_{\sigma} dS^\sigma > 0. \quad (776.1)$$

For an unnatural process,

$$\sum_{\alpha} dS^{\alpha} + \sum_{\sigma} dS^{\sigma} < 0. \quad (776\cdot2)$$

For a reversible process,

$$\sum_{\alpha} dS^{\alpha} + \sum_{\sigma} dS^{\sigma} = 0. \quad (776\cdot3)$$

*Isothermal Processes.*—For isothermal processes in a system at uniform temperature we have, in accordance with (5) and (6) :

For a natural process

$$q < d(TS) \quad w > dF. \quad (777\cdot1)$$

For an unnatural process

$$q > d(TS) \quad w < dF. \quad (777\cdot2)$$

For a reversible process

$$q = d(TS) \quad w = dF, \quad (777\cdot3)$$

where the Helmholtz free energy  $F$  is defined by (762), and its variation  $dF$  is given by (763).

*Equilibrium Conditions.*—In analogy with (48) and (50), one can obtain inter alia the two following conditions of equilibrium :

1. In any infinitesimal change in which no work is done on or by the system and in which no heat is absorbed or emitted by the system the entropy remains unchanged. In other words, for a given value of  $E$  the entropy  $S$  is a maximum.

2. In any infinitesimal change in which no work is done on or by the system and in which the temperature of the system is uniform and kept constant the Helmholtz free energy  $F$  remains unchanged. In other words, for a given value of  $T$  the Helmholtz free energy  $F$  is a minimum.

The general equilibrium conditions can be expressed in numerous other forms involving the various characteristic functions and choices of independent variables. Any one of these forms is equivalent to any other.

*Thermal Equilibrium.*—By a proof analogous to that of (67) we can, from the first form of our general equilibrium condition, show that the condition of thermal equilibrium between the various homogeneous phases  $\alpha, \beta, \dots$  and surface phases  $\sigma, \rho, \dots$  is that they should all be at the same temperature  $T$  or

$$T^{\alpha} = T^{\beta} = \dots = T^{\sigma} = T^{\rho} = \dots \quad (778)$$

*Chemical Equilibrium.*—By a proof analogous to that of (82) we can show that the condition that a surface phase  $\sigma$  should be

in equilibrium with a homogeneous phase  $\alpha$  as regards the species  $i$  is

$$\mu_i^\sigma = \mu_i^\alpha, \quad (779)$$

that is to say, that the species  $i$  should have the same chemical potential in the given surface phase as in the given homogeneous phase.

*Mechanical Equilibrium.*—Let  $\sigma$  denote the surface phase separating the two homogeneous phases,  $\alpha$  and  $\beta$  and let  $\delta\sigma$  denote an element of this surface phase so small that over it we may regard the two principal radii of curvature  $\rho_1$  and  $\rho_2$  as being constant. Now imagine an infinitesimal change consisting in a displacement of the element of surface  $\delta\sigma$  a distance  $d\nu$  in the direction of the normal to the surface pointing from  $\alpha$  to  $\beta$ , the temperature and total volume of the whole system being held constant. Then the increase  $dV^\alpha$  in the volume of the phase  $\alpha$  and  $dV^\beta$  in the volume of the phase  $\beta$  are clearly given by

$$dV^\alpha = A^{\delta\sigma} d\nu, \quad (780.1)$$

$$dV^\beta = -A^{\delta\sigma} d\nu, \quad (780.2)$$

where  $A^{\delta\sigma}$  is used to denote the area of the element  $\delta\sigma$ . The increase  $dA^{\delta\sigma}$  in the surface area of  $\delta\sigma$  is given by

$$dA^{\delta\sigma} = A^{\delta\sigma} \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) d\nu, \quad (781)$$

where each of the principal radii of curvature  $\rho_1$  and  $\rho_2$  is reckoned positive if the corresponding centre of curvature lies on the side of  $\sigma$  towards  $\alpha$ . Then, as the volume of the whole system remains unaltered there is no work done on or by the system, and the temperature being held constant, we may use the second form of the general equilibrium condition

$$dF = 0. \quad (782)$$

Assuming the deformation takes place without any transference of matter from one phase to another, and substituting from (763) into (782), we obtain

$$-P^\alpha dV^\alpha - P^\beta dV^\beta + \gamma^\sigma dA^\sigma = 0. \quad (783)$$

Now, substituting from (780), (781) into (783), we obtain finally

$$P^\alpha - P^\beta = \left( \frac{1}{\rho_1} + \frac{1}{\rho_2} \right) \gamma^\sigma. \quad (784)$$

In the case when the surface  $\sigma$  is plane, the radii of curvature  $\rho_1$  and  $\rho_2$  are infinite and (784) simplifies to

$$P^\alpha = P^\beta, \quad (785)$$

the same as the relation (75) obtained ignoring the surface phases.

In the case of a bubble in the form of a thin spherical film of liquid of internal and external radii  $r_i$  and  $r_e$  if  $P^i$  denote the pressure nearer to the centre than the film,  $P^e$  the pressure further from the centre than the film, and  $P'$  the pressure in the liquid film itself, we have, according to (784)

$$P^i - P' = \frac{2}{r_i}\gamma, \quad (786.1)$$

$$P' - P^e = \frac{2}{r_e}\gamma, \quad (786.2)$$

so that

$$P^i - P^e = \left(\frac{2}{r_i} + \frac{2}{r_e}\right)\gamma, \quad (787)$$

or, neglecting the difference between  $r_i$  and  $r_e$ ,

$$P^i - P^e = \frac{4}{r}\gamma, \quad (788)$$

*Determination of Surface Tension.*—The commonest method of determining the value of the surface tension  $\gamma$  depends on formula (784). This method is shown diagrammatically in Fig. 8. Two fluid phases,  $\alpha$  and  $\beta$ , are represented, the one shaded the other not shaded. They are separated partly by the plane surfaces  $AA''$  and  $A'A'''$ , and partly by the curved surface  $BB'$  in the capillary tube  $PP'QQ'$  of internal radius  $r$ . We may, with sufficient accuracy, regard the surface  $BB'$  as a segment of a sphere. Let the centre of this sphere be  $O$  and let  $\theta$  be the angle between  $OB$  and the horizontal  $OX$ , or alternatively the angle between the tangential phase to  $BB'$  at  $B$  and the wall of the vertical capillary tube. Then the radius of curvature of the surface  $BB'$  is  $\frac{r}{\cos \theta}$ .

Let  $P^o$  denote the pressure at the plane surfaces  $AA''$  and  $A'A'''$ . It will also be the pressure inside the capillary tube at the height  $AA'$ . Let the pressures at the height  $BB'$  be denoted by  $P^\alpha$  in the phase  $\alpha$  and by  $P^\beta$  in the phase  $\beta$ . Then

$$P^\alpha = P^o - \rho^\alpha gh, \quad (789.1)$$

$$P^\beta = P^o - \rho^\beta gh, \quad (789.2)$$



where  $\rho^\alpha$ ,  $\rho^\beta$  denote the densities of the phases  $\alpha$  and  $\beta$ ,  $g$  is the acceleration due to gravity, and  $h$  is the height  $AB$ . But, according to (784),

$$P^\beta - P^\alpha = 2 \frac{\cos \theta}{r} \gamma. \quad (790)$$

Comparing (789.1), (789.2) and (790), we obtain

$$2 \frac{\cos \theta}{r} \gamma = (\rho^\alpha - \rho^\beta)gh. \quad (791)$$

Thus, from measurement of  $\rho^\alpha$ ,  $\rho^\beta$ ,  $r$ ,  $\theta$ , and  $h$ , one can calculate  $\gamma$ . In the special case that  $\alpha$  is a liquid and  $\beta$  the vapour phase

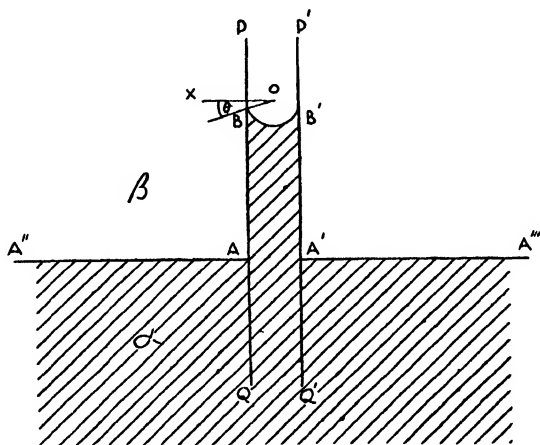


FIG. 8.

in equilibrium with it, it will be allowable to neglect  $\rho^\beta$ , compared with  $\rho^\alpha$  so that (791) simplifies to

$$2 \frac{\cos \theta}{r} \gamma = \rho^\alpha gh. \quad (792)$$

In the case that the surface  $BB'$  is concave towards the bottom, its radius of curvature will have the opposite sign, and so  $h$  will also have the opposite sign. That is to say, that  $BB'$  will lie below  $AA'$ .

*Vapour Pressure of Small Drops.*—Fig. 9 represents a small spherical drop and a portion of liquid in bulk, both at the same temperature. The composition at the interior  $\alpha$  of the drop is

also supposed to be identical with that at the interior  $\beta$  of the liquid in bulk. The chemical potentials  $\mu_i$  and so the partial vapour pressures  $p_i$  of the various components  $i$  will be equal at  $\alpha$  and  $\beta$  provided the total pressures  $P^\alpha$  at  $\alpha$  and  $P^\beta$  at  $\beta$  are equal. That is to say, the condition that the small drop and the liquid in bulk should be in chemical equilibrium as regards all the components, the temperature and internal compositions being the same, is

$$P^\alpha = P^\beta. \quad (793)$$

But when condition (793) is satisfied, the small drop and the liquid in bulk will not be at the same *external* pressures. For if  $r$  is the radius of the small drop, the pressures  $P^{\alpha'}$  at  $\alpha'$  just

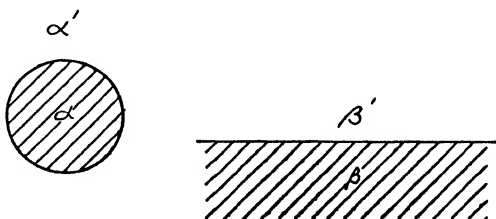


FIG. 9.

outside the surface of the drop and  $P^{\beta'}$  at  $\beta'$  just outside the surface of the liquid in bulk are according to (784) given by

$$P^{\alpha'} = P^\alpha - \frac{2}{r}\gamma, \quad (794.1)$$

$$P^{\beta'} = P^\beta. \quad (794.2)$$

Hence, at chemical equilibrium, according to (793), the departure from hydrostatic equilibrium is given by

$$P^{\beta'} - P^{\alpha'} = \frac{2}{r}\gamma. \quad (795)$$

If, on the other hand, we assume that the external pressures  $P^{\alpha'}$  and  $P^{\beta'}$  are equal, that is

$$P^{\alpha'} = P^{\beta'}, \quad (796)$$

then, according to (794), the pressure  $P^\alpha$  at the interior  $\alpha$  of the drop is greater than that  $P^\beta$  at the interior  $\beta$  of the liquid in bulk, according to

$$P^\alpha - P^\beta = \frac{2}{r}\gamma. \quad (797)$$

But if the pressure  $P^\alpha$  inside the drop is greater than that  $P^\beta$  inside the liquid in bulk, then according to (153) and (401) the chemical potential  $\mu_i$  and the partial vapour pressure  $p_i$  of each component  $i$  inside the drop will be greater than in the liquid in bulk. If we neglect the compressibility of the liquid and denote by  $p_i^\alpha$  and  $p_i^\beta$  the partial vapour pressures of the component  $i$  in the drop and in the liquid in bulk, then (401) leads to

$$RT \log \frac{p_i^\alpha}{p_i^\beta} = (P^\alpha - P^\beta) V_i. \quad (798)$$

Combining (798) with (797), we obtain finally,

$$RT \log \frac{p_i^\alpha}{p_i^\beta} = \frac{2}{r} \gamma V_i. \quad (799)$$

It need hardly be mentioned that, provided the surfaces are in chemical equilibrium with the interior of the liquid,  $p_i^\alpha$  and  $p_i^\beta$  are equal to the partial vapour pressures, not only in the interiors of the drop and the liquid in bulk, but also at the surfaces of the drop and the liquid in bulk.

*Energy Density and Entropy Density.*—The surface energy  $E^\sigma$  and the surface entropy  $S^\sigma$  are capacity factors, their values for a given state of the surface being proportional to its extent. For describing the properties of a surface phase independent of its extent it is convenient to use the surface energy density  $E^\sigma$  and the surface entropy density  $S^\sigma$  defined by

$$E^\sigma = E^\sigma A^\sigma, \quad (800.1)$$

$$S^\sigma = S^\sigma A^\sigma. \quad (800.2)$$

By substituting from (800) and (745), we can transform (751) to

$$dE^\sigma = TdS^\sigma + \sum_i \mu_i^\sigma d\Gamma_i^\sigma. \quad (801)$$

*Available Surface Energy.*—The product  $\gamma^\sigma A^\sigma$  is sometimes called the “available energy of the surface  $\sigma$ ”. Its variation is given by

$$d(\gamma^\sigma A^\sigma) = \gamma^\sigma dA^\sigma + A^\sigma d\gamma^\sigma, \quad (802.1)$$

or, combining this with (773),

$$d(\gamma^\sigma A^\sigma) = -S^\sigma dT^\sigma + \gamma^\sigma dA^\sigma - \sum_i n_i d\mu_i^\sigma. \quad (802.2)$$

*Variation of Surface Tension.*—By applying (802.2) to unit surface, we obtain for the variation of the surface tension

$$d\gamma^\sigma = -S^\sigma dT - \sum_i \Gamma_i^\sigma d\mu_i^\sigma. \quad (803)$$

As already mentioned, the values of the  $\Gamma_i^\sigma$  depend on the exact position of the geometrical surface  $\sigma$ . The sum  $\sum_i \Gamma_i^\sigma d\mu_i^\sigma$  occurring in (803) is, however, invariant with respect to changes in the position of the surface  $\sigma$ . For, suppose  $\sigma$  separates the homogeneous phases  $\alpha$  and  $\beta$ , and imagine the surface  $\sigma$  to be moved a distance  $\delta$  from  $\alpha$  towards  $\beta$ . Then, from the definition of  $\Gamma_i^\sigma$  it is easy to see that the new value of  $\Gamma_i^\sigma$  exceeds the old value by

$$\delta(C_i^\beta - C_i^\alpha), \quad (804.1)$$

where  $C_i^\alpha$ ,  $C_i^\beta$  are the volume concentrations of the species  $i$  in the homogeneous phases  $\alpha$  and  $\beta$ . But the equilibrium condition for the species  $i$  between the two homogeneous phases  $\alpha$ ,  $\beta$  and the surface phase  $\sigma$  is

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\sigma. \quad (804.2)$$

Hence, the new value of the sum  $\sum_i \Gamma_i^\sigma d\mu_i^\sigma$  exceeds the old value by

$$\delta \sum_i (C_i^\beta - C_i^\alpha) d\mu_i^\sigma = \delta \sum_i C_i^\beta d\mu_i^\beta - \delta \sum_i C_i^\alpha d\mu_i^\alpha. \quad (804.3)$$

But according to the Gibbs-Duhem relation (33) we have in either homogeneous phase

$$\sum_i C_i^\alpha d\mu_i^\alpha = 0, \quad (804.4)$$

$$\sum_i C_i^\beta d\mu_i^\beta = 0. \quad (804.5)$$

Substituting (804.4) and (804.5) into (804.3), we see that when the geometrical surface  $\sigma$  is moved the sum  $\sum_i \Gamma_i^\sigma d\mu_i^\sigma$  remains unchanged.

*Temperature Coefficient of Surface Tension.*—The behaviour of a surface phase is simplest in the case of a system of only one component. Let us suppose that the surface  $\sigma$  separates the two homogeneous phases  $\alpha$  and  $\beta$  consisting of one and the same single component. If the three phases  $\alpha$ ,  $\beta$ ,  $\sigma$  are in complete equilibrium and the surface  $\sigma$  is plane, the state of the system is completely determined by the temperature. The pressures of the two phases  $\alpha$  and  $\beta$ , which must be equal, will depend on the temperature according to (272). The state of the surface phase will then be completely determined by the necessity that the chemical potential  $\mu^\sigma$  should have the same value as those  $\mu^\alpha$  and  $\mu^\beta$  in the homogeneous phases. If according to (747) we so choose

the hypothetical geometrical surface that the surface concentration  $\Gamma^\sigma$  is always zero, then (803) becomes simply

$$d\gamma^\sigma = -S^\sigma dT, \quad (805)$$

or,

$$\frac{d\gamma^\sigma}{dT} = -S^\sigma. \quad (806)$$

But with this choice of the position of the geometrical surface, if we suppose the area of the surface phase increased by unity by an alteration in the shapes of the homogeneous phases, there will by definition be no change in the quantities  $n_i^\alpha$ ,  $n_i^\beta$ ,  $n_i^\sigma$ . It follows that the increase of entropy of the whole system will be simply  $S^\sigma$ . If the surface be increased reversibly, the heat absorbed will therefore be  $TS^\sigma$ . We may therefore write (806) in the form

$$\frac{d\gamma^\sigma}{dT} = -\frac{L^\sigma}{T}, \quad (807)$$

where  $L^\sigma$  is the heat of reversible formation of unit area of the surface phase.

The dependence on the temperature of the surface tension in systems of several components is considerably more complicated. We shall confine ourselves to a consideration of the important case of a surface phase  $\sigma$  forming the boundary between a liquid solution  $\alpha$  and a vapour phase  $\beta$  in equilibrium with  $\alpha$ . For variations of the three phases  $\alpha$ ,  $\beta$ ,  $\sigma$  we have, according to (152), (153) and (803)

$$d\mu_i^\alpha = -S_i^\alpha dT + V_i^\alpha dP + D\mu_i^\alpha, \quad (808.1)$$

$$d\mu_i^\beta = -S_i^\beta dT + V_i^\beta dP + D\mu_i^\beta, \quad (808.2)$$

$$d\gamma^\sigma = -S^\sigma dT - \sum_i \Gamma_i^\sigma d\mu_i^\sigma. \quad (808.3)$$

We also have the equilibrium conditions for each species  $i$

$$\mu_i^\alpha = \mu_i^\beta = \mu_i^\sigma. \quad (809)$$

For temperature variations at constant composition of the solution we have, by definition of the operator  $D$ ,

$$D\mu_i^\alpha = 0 \quad (810)$$

and so from (808.1), (808.3) and (810)

$$d\gamma^\sigma = -S^\sigma dT + \sum_i \Gamma_i^\sigma S_i^\alpha dT - \sum_i \Gamma_i^\sigma V_i^\alpha dP. \quad (811)$$

But according to the phase rule, for constant composition of the solution, the temperature and pressure at which there is equilibrium between the solution and vapour are not independently variable. In fact, we have

$$P = \sum_k p_k, \quad (812.1)$$

where the partial vapour pressures  $p_k$  of the various species  $k$  depend on the temperature according to

$$dp_k = \frac{S_k^\beta - S_k^\alpha}{V_k^\beta - V_k^\alpha} dT. \quad (812.2)$$

Substituting from (812.1) and (812.2) into (811), we obtain finally

$$\frac{d\gamma^\sigma}{dT} = -S^\sigma + \sum_i \Gamma_i^\sigma S_i^\alpha - \sum_i \Gamma_i^\sigma V_i^\alpha \sum_k \frac{S_k^\beta - S_k^\alpha}{V_k^\beta - V_k^\alpha}. \quad (813)$$

In the denominator of the terms of the last sum  $V_k^\alpha$  the partial molar volume in the solution is very small compared with  $V_k^\beta$ , the partial molar volume in the vapour, and so may be omitted. No further simplification of this rather complicated formula appears possible in general. Although the terms of the last sum contain the small factor  $V_i^\alpha/V_k^\beta$ , the remaining factors containing the difference  $S_k^\beta - S_k^\alpha$  may make the whole sum of the same order of magnitude as the first terms of

$$-S^\sigma + \sum_i \Gamma_i^\sigma S_i^\alpha.$$

If we could have the vapour phase  $\beta$  at a different pressure  $P^\beta$  from that  $P^\alpha$  of the solution, then the phase rule would allow temperature variations at constant composition of  $\alpha$  and constant pressure  $P^\alpha$ . In this case,  $dP$  would be zero in formula (811), and so we should have

$$\frac{d\gamma^\sigma}{dT} = -S^\sigma + \sum_i \Gamma_i^\sigma S_i^\alpha. \quad (814)$$

This formula is much simpler than (813), but it is difficult to see how the conditions for its validity could be realised in practice. For to maintain the two phases  $\alpha$  and  $\beta$  at different pressures it is generally necessary to separate them by a membrane permeable to the vapour only, and in that case we should not have a free surface  $\sigma$  connecting the phases  $\alpha$  and  $\beta$ .

*Adsorption Equilibrium.*—For variations at constant temperature (808.3) simplifies to

$$\begin{aligned} d\gamma^\sigma &= - \sum_i \Gamma_i^\sigma D\mu_i^\alpha \\ &= - \sum_i \Gamma_i^\sigma RTD \log p_i^\beta, \end{aligned} \quad (815)$$

where  $p_i^\beta$  is the partial pressure of the species  $i$  in the vapour phase  $\beta$ . Now the partial vapour pressures are not all independent owing to the Duhem-Margules relation (387)

$$\sum_i N_i D \log p_i = 0. \quad (816)$$

It is therefore convenient to regard the partial vapour pressures  $p_s$  of the various solute species  $s$  as independent variables, and the partial vapour pressure of the solvent as a function of these. Making this choice of independent variables, and at the same time choosing the hypothetical geometrical surface corresponding to  $\sigma$  so that the surface concentration  $\Gamma_0^\sigma$  of the solvent species is always zero, (815) becomes

$$d\gamma^\sigma = - \sum_s \Gamma_s^\sigma RTD \log p_s. \quad (817)$$

This is Gibbs' adsorption formula. In terms of the mole fractions and activity coefficients of the solute species, it may be written in the alternative form

$$d\gamma^\sigma = - \sum_s \Gamma_s^\sigma RTD \log N_s f_s. \quad (818)$$

Further simplification of (818) is, in general, not possible. In the special case, however, of only one solute species it becomes

$$d\gamma^\sigma = - \Gamma_s RT d \log N_s f_s, \quad (819)$$

which may be written in the alternative form

$$\Gamma_s = - \frac{1}{RT} \frac{\partial \gamma}{\partial \log N_s f_s}. \quad (820)$$

For the general case of several solute species, on the other hand, if the mole fraction of the one species 1 be varied, while those of all the other solute species be kept unchanged, we have

$$- \frac{1}{RT} \frac{\partial \gamma}{\partial N_1} = \frac{\Gamma_1}{N_1} + \frac{\Gamma_1 \partial \log f_1}{\partial N_1} + \sum_s \Gamma_s \frac{\partial \log f_s}{\partial N_1}. \quad (821)$$

Since, in general, alteration of  $N_1$  causes alteration not only of  $f_1$  but also of all the  $f_s$ , further simplification is impossible.

Only in the exceptional case of an ideal solution all the activity coefficients are unity and (818) or (821) becomes

$$d\gamma = - \Gamma_s RT d \log N_s \quad (822)$$

or

$$\Gamma_s = - \frac{1}{RT} \frac{\partial \gamma}{\partial \log N_s} \quad (823)$$

From (817) we see that addition to the pure solvent of a solute that is positively adsorbed at the surface ( $\Gamma_s$  positive) produces a decrease of the surface tension  $\gamma$ , while addition of a substance that is negatively adsorbed ( $\Gamma_s$  Negative) produces an increase of the surface tension.

*Insoluble Films.*—The treatment of surface phases so far given is the classical one due to Gibbs. The usefulness of the formulæ presupposes that the total quantity of any species present in any surface phase is very small compared with the quantity present in the contiguous homogeneous phases. The

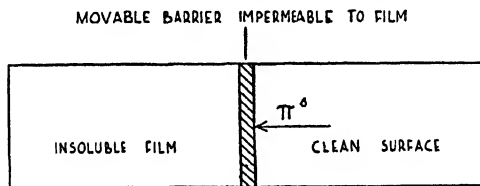


FIG. 10.

contrary case was referred to by Gibbs as of "secondary interest". Of recent years the experiments of Pockels, Rayleigh, Devaux, Marcelin, Langmuir and Adam have brought into prominence surface phases of a quite different type. These experiments are concerned with the behaviour of minute quantities of various substances at the surface of a single underlying liquid, usually water. These substances are so slightly soluble in the liquid phase and so involatile that during the time of an experiment the quantity that can dissolve or evaporate is quite negligible compared with the quantity that remains at the surface. As regards the quantity at the surface phase, this is so small that the film is actually only one molecule thick.

The experimental and theoretical treatment most suitable for thermodynamic discussion is due to Adam. His experimental measurements are shown schematically in Fig. 10. Part of the liquid surface covered with the insoluble film is separated from a clean surface by a movable barrier impermeable to the film. The quantity measured is the force per unit length of the barrier



required to prevent the insoluble film from expanding. This quantity, which we shall denote by  $\Pi^\sigma$ , has been named by Adam the "two-dimensional osmotic pressure" of the surface film. This name is appropriate, inasmuch as it is the excess force per unit length or the excess "two-dimensional pressure" to which the surface film must be subjected in order that the film and the clean surface may be in equilibrium as regards the underlying liquid. For, obviously, as regards the underlying liquid there is equilibrium between the film and the homogeneous phase and likewise between the clean surface and the homogeneous phase. Consequently, there must be equilibrium between the film and the clean surface.

A surface phase  $\sigma$  of the type in question is completely defined by the nature of the underlying liquid, which we shall denote by the suffix  $o$ , by the temperature  $T$  of the whole system, by the surface area  $A^\sigma$  of the film, and by the number of moles  $n_i$  of each species  $i$  other than the species  $o$ . Corresponding to each extensive quantity  $n_i^\sigma$  is the intensive quantity  $\Gamma_i^\sigma$ , called the surface concentration of  $i$ , and defined by

$$n_i^\sigma = \Gamma_i^\sigma A^\sigma. \quad (824)$$

In the usual experiments there is only one insoluble species  $i$ , but there seems no reason to restrict the treatment to this case. The quantity  $\Gamma_o^\sigma$ , which one might call the surface concentration of the species  $o$ , is not an independent variable, as the state of this species in the surface phase  $\sigma$  is regulated by the condition of equilibrium (779) with the homogeneous phase

$$\mu_o^\sigma = \mu_o^\alpha. \quad (824)$$

Moreover, the value of the surface concentration  $\Gamma_o^\sigma$  is to some extent arbitrary, depending on the exact position chosen for the geometrical surface corresponding to the surface phase. By a suitable choice we can make  $\Gamma_o^\sigma$  always zero. The surface concentrations of the insoluble species  $\Gamma_i^\sigma$ , on the other hand, can be varied independently, and their values are known directly from the total number of moles  $n_i^\sigma$  of the species present and the surface area  $A^\sigma$  of the film.

For the sake of simplicity we may suppose both the species  $o$  and the species  $i$  so slightly volatile that the quantity of matter and so also of energy and entropy in the vapour phase is negligible.

In this case, the energy  $E^\sigma$  and entropy  $S^\sigma$  of the surface phase are defined in terms of the energy  $E$  and entropy  $S$  of the whole system by

$$E = E^\alpha + E^\sigma, \quad (825.1)$$

$$S = S^\alpha + S^\sigma, \quad (825.2)$$

where  $E^\sigma$ ,  $S^\sigma$  are the energy and entropy computed for the underlying liquid on the assumption that it remained homogeneous right to the surface. With these definitions of the surface energy and surface entropy, and with the geometrical surface so chosen that  $\Gamma_0^\sigma$  is zero, we have, in analogy with (751), the differential relation

$$dE^\sigma = T^\sigma dS^\sigma + \gamma^\sigma dA^\sigma + \sum_i \mu_i^\sigma dn_i^\sigma. \quad (826)$$

Integrating this, keeping the intensity factors  $T^\sigma$ ,  $\gamma^\sigma$  and  $\mu_i^\sigma$  constant, we obtain

$$E^\sigma = T^\sigma S^\sigma + \gamma^\sigma A^\sigma + \sum_i \mu_i^\sigma n_i^\sigma. \quad (827)$$

Differentiating (827) and comparing with (826), we obtain

$$-S^\sigma dT^\sigma - A^\sigma d\gamma^\sigma - \sum_i n_i^\sigma d\mu_i^\sigma = 0. \quad (828)$$

Applying (828) to unit area of the surface, and confining ourselves to variations at constant temperature, we obtain

$$d\gamma^\sigma = - \sum_i \Gamma_i^\sigma D\mu_i^\sigma. \quad (829)$$

This formula differs slightly from (815), because owing to the effectively complete insolubility and involatility of the film, we cannot replace the values of the chemical potential  $\mu_i^\sigma$  in the surface phase by their values in either the underlying liquid phase or the vapour phase. In fact, the determination of the chemical potentials of the species  $\mu_i^\sigma$  in the film is best made by using (829). In the experimental procedure shown diagrammatically in Fig. 10, the force per unit length of the barrier or the "two-dimensional osmotic pressure"  $\Pi^\sigma$  is given by

$$\Pi^\sigma = \gamma^\circ - \gamma^\sigma, \quad (830)$$

where  $\gamma^\sigma$  is the surface tension of the film and  $\gamma^\circ$  that of the clean surface. Hence, for a given underlying liquid at given temperature

$$d\Pi^\sigma = -d\gamma^\sigma. \quad (831)$$

Substituting from (831) into (829), we obtain

$$d\Pi^\sigma = \sum_i \Gamma_i^\sigma D\mu_i^\sigma. \quad (832)$$

In actual practice, measurements have usually been made on films consisting of only one species  $i$  other than the underlying liquid. In this case, (832) simplifies to

$$d\Pi^\sigma = \Gamma_i^\sigma d\mu_i^\sigma. \quad (833)$$

It was suggested by Langmuir in 1917 that the films might be classified according to the relation between  $\Pi^\sigma$  and  $\Gamma^\sigma$  as two-dimensional solids, liquids and vapours. That this is actually the case has been proved experimentally by Adam in 1926.

In two-dimensional gaseous films the equilibrium two-dimensional pressure  $\Pi^\sigma$  increases with the surface concentration  $\Gamma_i^\sigma$ . Adam has shown both theoretically and experimentally that the limiting law for low surface concentrations and low equilibrium pressures of gaseous films is

$$\Pi^\sigma = RT\Gamma_i^\sigma, \quad (834)$$

which is the analogue of the equation of state (198)

$$P = RTc_i, \quad (835)$$

of a perfect gas. Substituting (834) into (833), we have

$$RTd\Gamma_i^\sigma = \Gamma_i^\sigma d\mu_i^\sigma, \quad (836)$$

which gives on integration,

$$\mu_i^\sigma = \mu_i^\circ + RT \log \Gamma_i^\sigma, \quad (837)$$

where  $\mu_i^\circ$  depends on the temperature and nature of the underlying liquid but is independent of the surface concentration  $\Gamma_i^\sigma$  of the film. Formula (837) is analogous to the formula for the chemical potential of a perfect gas.

If we define the partial molar area  $A_i^\sigma$  of the species  $i$  in the film by

$$A_i^\sigma = \left( \frac{\partial A^\sigma}{\partial n_i^\sigma} \right)_{T, \gamma^\sigma}, \quad (838)$$

then the total area  $A^\sigma$  is given by

$$A_i^\sigma = \sum_i n_i^\sigma A_i^\sigma, \quad (839)$$

where the summation does not include the species of the underlying liquid. Applying (839) to unit surface area, we obtain

$$\sum_i \Gamma_i^\sigma A_i^\sigma = 1. \quad (840)$$

In the particular case of only one species in the film other than the underlying liquid, (840) becomes simply

$$\Gamma_i^\sigma A_i^\sigma = 1. \quad (841)$$

In terms of the partial molar area  $A_i^\sigma$  formula (834) becomes

$$\Pi^\sigma A_i^\sigma = RT, \quad (842)$$

the analogue of (323) for a perfect gas. Formula (842) may be expected to hold for small surface concentrations of films containing more than one species apart from the underlying liquid.

For two-dimensional liquid films, as compared to two-dimensional gaseous films, the partial molar area  $A_i^\sigma$  decreases considerably less with increase of the pressure  $\Pi^\sigma$ . If we write

$$A_i^\sigma = A_i^\circ(1 - \kappa_i^\sigma \Pi^\sigma), \quad (843)$$

where  $A_i^\circ$  is independent of  $\Pi^\sigma$ , then the two-dimensional compressibility  $\kappa_i^\sigma$  is small compared with  $1/\Pi^\sigma$ , and varies much more slowly with the two-dimensional pressure than in the case of a two-dimensional gas. The value of  $\kappa_i^\sigma$  may not, however, be assumed independent of the two-dimensional pressure.

Just as the external pressure on a liquid cannot be less than its vapour pressure, so there is a minimum value of  $\Pi^\sigma$  for a two-dimensional liquid film. This is the two-dimensional "vapour pressure"  $p^\sigma$  of the liquid film. If we commence with a liquid film under compression and gradually decrease the pressure  $\Pi^\sigma$  exerted on the barrier, the molar area  $A_i^\sigma$  will increase only slowly, according to (843), until the pressure reaches the value  $p^\sigma$ , the two-dimensional vapour pressure. Further expansion of the film then takes place at the constant pressure  $p^\sigma$ . This is two-dimensional evaporation, and the film is no longer homogeneous, but partly liquid and partly vapour. When the area of the film has become so great that the film is completely gaseous, further expansion will be accompanied by a fall of pressure according to (842).

#### NOTES AND REFERENCES

*Surface Phases.*—The only exact thermodynamic treatment of surfaces, either original or otherwise, is that given by Gibbs, *vide* "Collected Works". An excellent elementary treatment is given in Adam's "Physics and Chemistry of Surfaces." The dependence of the values of the  $\Gamma_i$  on the exact position assigned to the hypothetical geometrical surface has been discussed in detail by Guggenheim and Adam in *Proc. Roy. Soc., A*, **139**, 218 (1933).

*Insoluble Films.*—A review of insoluble surface films with full references to the literature is given by Adam in *Kolloid-Zeitschrift*, **57**, 125 (1931). For more detailed discussion, see Adam's "Physics and Chemistry of Surfaces".

## CHAPTER XIII

### RADIATION

*Thermodynamic Functions.*—Space containing no matter may still contain energy in the form of radiation. If this is in thermal equilibrium with its surroundings, it will have a definite temperature the same as that of the surroundings.

This system being of one phase and no components has, according to the phase rule, only one degree of freedom. Thus apart from its size its state is completely determined by either the temperature or the pressure, but these are not independently variable. We therefore choose as independent variables the temperature and the volume. The corresponding characteristic function is the Helmholtz free energy  $F$ .

The energy, the entropy and the Helmholtz free energy being capacity factors are proportional to the volume, also a capacity factor. We may therefore write

$$E = EV \quad (844\cdot1)$$

$$S = SV \quad (844\cdot2)$$

$$F = FV, \quad (844\cdot3)$$

where the energy density  $E$ , the entropy density  $S$  and the Helmholtz free energy density  $F$  depend only on the temperature.

*Thermodynamic Relations.*—According to (166), (24) and (844) the quantities  $E$ ,  $S$ ,  $F$  are related by

$$F = E - TS, \quad (845)$$

$$\frac{dF/T}{dT} = -\frac{E}{T^2}. \quad (846)$$

According to (27·2) and (844·3) the pressure is given by,

$$P = -\left(\frac{\partial F}{\partial V}\right)_T = -F. \quad (847)$$

*Stefan's Law.*—According to either the classical electromagnetic theory or the quantum theory of radiation the pres-

sure  $P$  of the radiation is one-third of its energy density  $E$ , that is to say,

$$P = \frac{1}{3}E. \quad (848)$$

Substituting (847) into (848), we obtain

$$F = -\frac{1}{3}E. \quad (849)$$

Now substituting from (849) into (846), we obtain

$$\frac{dE/T}{dT} = 3 \frac{E}{T^2}. \quad (850)$$

Integration of (850) gives

$$E = \alpha T^4, \quad (851)$$

where  $\alpha$  is a universal constant. Formula (851) is known as the Stefan-Boltzmann law and  $\alpha$  is called the Stefan constant. Its value is given by the quantum theory.

From (851), (848), (849), (845) we obtain immediately

$$P = -F = \frac{1}{3}\alpha T^4, \quad (852)$$

$$S = \frac{4}{3}\alpha T^3, \quad (853)$$

or

$$TS = 4P. \quad (854)$$

*Adiabatic Changes.*—If the volume occupied by a given quantity of radiation is altered and the radiation remains in thermal equilibrium, its temperature will change. For such a reversible adiabatic change we have, according to (34.3),

$$S = \text{constant}, \quad (855)$$

or according to (844.2)

$$SV = \text{constant}. \quad (856)$$

From (856), (854), (852), we deduce

$$PV \propto T \quad (857.1)$$

$$P \propto T^4 \quad (857.2)$$

$$VT^3 = \text{constant} \quad (857.3)$$

$$PV^{\frac{4}{3}} = \text{constant}. \quad (857.4)$$

From a comparison of (857) and (220), (221), (222) it appears that the relations for a reversible adiabatic change in radiation

are the same as in a perfect gas for which the ratio of the heat capacities has the constant value  $\frac{4}{3}$ . This parallelism is, however, accidental, for the ratio of the heat capacities of radiation is not  $\frac{4}{3}$ . In fact for radiation

$$C_V = \left(\frac{\partial E}{\partial T}\right)_V = T\left(\frac{\partial S}{\partial T}\right)_V = \frac{4}{3}\alpha T^3 V, \quad (858.1)$$

while

$$C_P = T\left(\frac{\partial S}{\partial T}\right)_P = \infty, \quad (858.2)$$

since no increase of  $S$ , however great, can increase  $T$  without simultaneously increasing  $P$ .

*Gibbs Free Energy.*—As already mentioned the temperature and pressure cannot be chosen as independent variables for radiation. It is interesting to observe that the Gibbs Free Energy  $G$ , which is the characteristic function corresponding to such a choice of independent variables, has the value zero. For by the definitions (21), (24) and (25)

$$G = F + PV, \quad (859)$$

and so using (844.3) and (847)

$$G = 0. \quad (860)$$

## NOTES AND REFERENCES

*Radiation.*—An exhaustive treatment of the thermodynamics and statistical mechanics of radiation is to be found both in Fowler's "Statistical Mechanics" and in Brillouin's "Die Quantenstatistik".

## CHAPTER XIV

### SO-CALLED THIRD LAW AND CHEMICAL CONSTANTS

*Dependence on Temperature of Heat Content, Entropy and Gibbs Free Energy Changes in Reactions.*

If we use the operator  $\Delta$  to denote the excess of the final over the initial values in any isothermal process (defined by the composition of each phase in the initial and final state) occurring at a constant pressure, then we have according to (144)

$$\frac{\partial}{\partial T} \Delta H = \Delta C_P, \quad (861)$$

and according to (142)

$$\frac{\partial}{\partial T} \Delta S = \frac{\Delta C_P}{T}, \quad (862)$$

and according to (171)

$$\frac{\partial}{\partial T} \frac{\Delta G}{T} = - \frac{\Delta H}{T^2}. \quad (863)$$

Integration of (861) and (862) from a standard temperature  $T^\circ$  to the variable temperature  $T$  leads to

$$\Delta H = \Delta H^\circ + \int_{T^\circ}^T \Delta C_P dT, \quad (864)$$

$$\Delta S = \Delta S^\circ + \int_{T^\circ}^T \frac{\Delta C_P}{T} dT. \quad (865)$$

Combining (864) and (865) with the definition of  $G$  (25) we obtain

$$\Delta G = \Delta H^\circ - T \Delta S^\circ + \int_{T^\circ}^T \Delta C_P dT - T \int_{T^\circ}^T \frac{\Delta C_P}{T} dT \quad (866.1)$$

where the index 0 refers to the value of the function at the



standard temperature  $T^\circ$ . By integration by parts (866) can be transformed to

$$\Delta G = \Delta H^\circ - T\Delta S^\circ - T \int_{T^\circ}^T \frac{dT}{T^2} \int_{T^\circ}^T \Delta C_P dT', \quad (866\cdot2)$$

which is the integral of (863). By algebraic transformation this becomes

$$\begin{aligned} \Delta G = \Delta H^{\circ'} - T\Delta S^{\circ'} + \Delta C_P^\circ T(1 - \log T) \\ - T \int_{T^\circ}^T \frac{dT}{T^2} \int_{T^\circ}^T (\Delta C_P - \Delta C_P^\circ) dT', \end{aligned} \quad (867\cdot1)$$

$$\begin{aligned} \text{where} \quad \Delta H^{\circ'} &= \Delta H^\circ - \Delta C_P^\circ T^\circ, & (867\cdot2) \\ \Delta S^{\circ'} &= \Delta S^\circ - \Delta C_P^\circ \log T^\circ. & (867\cdot3) \end{aligned}$$

*Choice of Standard Temperature.*—In formulæ (864), (865) and (867·1) it would at first seem that the most natural value to choose for the standard temperature is zero, in which case  $\Delta H^\circ$ ,  $\Delta S^\circ$  and  $\Delta C_P^\circ$  would be the values of  $\Delta H$ ,  $\Delta S$  and  $\Delta C_P$  at the absolute zero of temperature. Unfortunately, however, measurements cannot be made at the absolute zero of temperature. In particular we cannot measure the values of the heat capacities  $C_P$  in the immediate neighbourhood of the absolute zero, and so we cannot evaluate the integrals occurring in (864), (865) and (867·1) for  $T^\circ$  zero. If, however, these integrals be evaluated for various small values of  $T^\circ$ , then as  $T^\circ$  is decreased their values as determined by experiment always converge towards a well-defined limit. We may therefore write

$$\Delta H = \Delta H^\circ + \int_0^T \Delta C_P dT, \quad (868)$$

$$\Delta S = \Delta S^\circ + \int_0^T \frac{\Delta C_P}{T} dT, \quad (869)$$

$$\begin{aligned} \Delta G = \Delta H^\circ - T\Delta S^{\circ'} + \Delta C_P^\circ T(1 - \log T) \\ - T \int_0^T \frac{dT}{T^2} \int_0^T (\Delta C_P - \Delta C_P^\circ) dT' \end{aligned} \quad (870)$$

where  $\Delta H^\circ$ ,  $\Delta S^{\circ'}$  and  $\Delta C_P^\circ$  are independent of the temperature, and the integral sign  $\int_0^T$  denotes the limit towards which the integral  $\int_{T^\circ}^T$  converges as the value of  $T^\circ$  is decreased.

*Heat Capacities at Low Temperatures.*—We know both from quantum theory and from experiment that at low temperatures the heat capacity  $C_P$  of any phase tends to a finite

or zero limit  $C_P^\circ$ , as the temperature is reduced, in such a manner that

$$\frac{C_P - C_P^\circ}{T^2} \rightarrow 0. \quad (871)$$

This behaviour of the heat capacity of any phase persists down to the lowest temperatures attainable by any methods at present known, that is down to temperatures of the order of 1 degree. It is for this reason that the integrals in (868), (869) and (870) converge to definite limits as  $T^\circ$  is decreased, and it is to these limits that the integrals denoted by  $\int_0^x$  refer.

There are, however, theoretical reasons based on quantum theory for believing that at very much lower temperatures, possibly of the order of one thousandth of a degree, the heat capacity  $C_P$  of a phase would in certain cases acquire a value differing finitely from  $C_P^\circ$ . The difference between  $C_P$  and  $C_P^\circ$  at these minute temperatures would affect the value of  $\Delta H$  negligibly, but might well make a finite difference to the values of  $\Delta S$  and  $\Delta G$  owing to the integrals containing the factors  $\frac{1}{T}$  and  $\frac{1}{T^2}$  which are very large in the neighbourhood of the absolute zero. Such temperatures, however, lie far below the reach of any experimental refinements yet conceivable, and it appears improbable that they will ever be reached at least in the foreseeable future.

Owing to this possible complication in the behaviour of some of the heat capacities  $C_P$  at unattainably low temperatures, it is not strictly correct to refer to  $\Delta H^\circ$  and  $\Delta S^\circ$  as the values of  $\Delta H$  and  $\Delta S$  at the absolute zero. They are the limits to which  $\Delta H$  and  $\Delta S$  tend when the experimental data at the lowest attainable temperatures are extrapolated. Alternatively we may call  $\Delta H^\circ$  and  $\Delta S^\circ$  the values of  $\Delta H$  and  $\Delta S$  in an idealised state in which all the heat capacities  $C_P$  had retained their value  $C_P^\circ$  right down to the absolute zero. For the sake of brevity we shall refer to such a state as the "idealised absolute zero".

As mentioned above any deviations of  $C_P$  from  $C_P^\circ$  at unattainably low temperatures will be of such a magnitude as to affect the value of  $\Delta H$  negligibly. It is therefore permissible to regard  $\Delta H^\circ$  as the value of  $\Delta H$  at either the true absolute zero or the idealised absolute zero. But  $\Delta S^\circ$  is the value of  $\Delta S$  at the idealised absolute zero, and may differ finitely from the value of  $\Delta S^\circ$  at the true absolute zero.

*Bearing of Thermodynamics and of Statistical Mechanics.*—If we consider formulæ (868), (869) and (870) from a purely

thermodynamic point of view, we can deduce the equilibrium conditions for the given process at any temperature in terms of the values of  $\Delta H^\circ$  and  $\Delta S^\circ$ , but we can predict nothing concerning the values of  $\Delta H^\circ$  and  $\Delta S^\circ$  themselves. Statistical mechanics on the other hand is able to predict the value of  $\Delta S^\circ$  from a knowledge of the nature of the quantum states of lowest energy in each phase. We shall consider in detail only the thermodynamic applications of formulæ (868), (869), (870). As regards the statistical mechanical aspect, we shall merely give a brief outline of the kind of predictions that can be made concerning  $\Delta S^\circ$  and shall give a few important illustrative examples.

*So-called Third Law of Thermodynamics.*—Whilst postponing until a later stage of our discussion the more exact formulation of the statistical mechanical predictions, we may state here that for reactions involving only pure crystalline phases the value predicted for  $\Delta S^\circ$  is *often but not always* zero. Until fairly recently it was believed that for all reactions involving only pure crystalline phases  $\Delta S^\circ$  was zero. This statement, now known to be too general, was often referred to as the "Third Law of Thermodynamics".

*Reactions between Crystalline Phases.*—For crystalline phases the value of  $C_P^\circ$  to which  $C_P$  tends at the lowest temperatures attainable is zero and so (870) simplifies to

$$\Delta G = \Delta H^\circ - T\Delta S^\circ - T \int_0^T \frac{dT'}{T'^2} \Delta C_P dT'. \quad (872)$$

Moreover, at the lowest temperatures attainable  $C_P$  tends to zero like  $T^3$  so that the relation (871) is fulfilled. For each crystalline phase we can therefore evaluate the integral

$$\int_0^T \frac{dT'}{T'^2} C_P dT' \quad (873)$$

with confidence, provided the heat capacity has been measured down to low temperatures.

For a reaction between crystalline phases at a given pressure,  $\Delta H^\circ$  and  $\Delta S^\circ$  are simply constants for the given reaction. If the value of  $\Delta S^\circ$  is known from quantum theory, then according to (868) and (872)  $\Delta G$  can be computed at any temperature from a single measurement of  $\Delta H$  at any one temperature combined with measurements of the various  $C_P$  at all temperatures down to those where  $C_P$  is decreasing with the cube of the temperature.

Then knowing the value of  $\Delta G$  for the given reaction as a function of the temperature, we can predict at what temperature

its value will be zero and at this temperature the various phases will be in equilibrium.

*Evaporation from Pure Crystal.*—For the reaction consisting simply of evaporation from a crystal at a given pressure to the vapour phase at a variable pressure  $P$ , formula (870) is according to (215) or (216) equivalent to

$$\Delta\mu = \Delta H^\circ - T\Delta S^\circ + C_P^\circ T(1 - \log T) - T \int_0^T \frac{dT'}{T'^2} \int_0^{T'} (\Delta C_P - C_P^\circ) dT'' + RT \log P, \quad (874)$$

where the operator  $\Delta$  denotes the excess of a value in the vapour phase over its value in the crystal phase,  $C_P^\circ$  is the value of  $C_P$  at the idealised absolute zero for the vapour,  $S^\circ$  in the crystal is the same as  $S^\circ$  divided by the number of moles in the crystal, while  $S^\circ$  in the vapour is a constant independent of both temperature and pressure.<sup>1</sup> As already mentioned the value of  $C_P^\circ$  for the crystal is zero. The condition for equilibrium between the vapour and the crystal at the given temperature is

$$\mu^s = \mu^g, \quad (875)$$

where the indices  $s$  and  $g$  refer respectively to the crystal (solid) state and the vapour (gaseous) state. Substituting from (874) into (875) we obtain for the equilibrium vapour pressure  $p$  of the crystal

$$\log p = -\frac{\Delta H^\circ}{RT} + \frac{C_P^\circ}{R} \log T + \int_0^T \frac{dT'}{T'^2} \int_0^{T'} \frac{\Delta C_P - C_P^\circ}{R} dT'' + \frac{\Delta S^\circ - C_P^\circ}{R}. \quad (876)$$

*Vapour Pressure Constant.*—The integration constant in (876) is usually called the “chemical constant” of the particular species of which the crystal is composed and is denoted by the symbol  $i$ . Fowler suggests that a more suitable name would be the “vapour pressure constant”. This constant  $i$  is defined by

$$i = \frac{\Delta S^\circ - C_P^\circ}{R}. \quad (877)$$

*Equilibria between Crystalline Phases and Vapour Phase.*—The most general kind of reaction involving crystalline phases and vapours may be written formally

$$\sum_{i=1}^r \lambda_i S_i + \sum_{i=r+1}^s \lambda_i S_i = 0, \quad (878)$$

<sup>1</sup> The relation between  $S^{\circ'}$  and  $S^\circ$  for the vapour is not

$$S^{\circ'} = nS^\circ,$$

but

$$S^{\circ'} = nS^\circ - nR \log P.$$

In the crystal

$$S^{\circ'} = S^\circ = nS^\circ.$$

where  $S_1, \dots, S_r$  denote moles of the chemical species  $1, \dots, r$  in the crystalline state and  $S_{r+1}, \dots, S_s$  denote moles of the chemical species  $r+1, \dots, s$  in the vapour state. The  $\lambda_i$  are small integers, *positive* for the *products* and *negative* for the *reactants* in the reaction. For such a reaction proceeding in the *forward direction* the increase in the Gibbs free energy is given by

$$\begin{aligned}\Delta G &= \sum_{i=1}^r \lambda_i \mu_i + \sum_{i=r+1}^s \lambda_i \mu_i \\ &= \Delta G^s + \sum_{i=r+1}^s \lambda_i (\mu_i^g - \mu_i^s),\end{aligned}\quad (879)$$

where  $\Delta G^s$  is the value of  $\Delta G$  for the same chemical reaction taking place entirely between pure crystalline phases, and  $\mu_i^g$ ,  $\mu_i^s$  are respectively the chemical potentials of the species  $i$  in the vapour and in the pure crystalline state. Combining formulæ (872), (874) and (879) we obtain

$$\begin{aligned}\Delta G &= \Delta H^\circ - \sum_{i=r+1}^s \lambda_i C_i^\circ T \log T - T \int_0^T \frac{dT'}{T'^2} \int_0^T \sum_{i=1}^r \lambda_i C_i dT' \\ &\quad - T \int_0^T \frac{dT'}{T'^2} \int_0^T \sum_{i=r+1}^s \lambda_i (C_i - C_i^\circ) dT' + RT \sum_{i=r+1}^s \lambda_i \log p_i \\ &\quad - T \sum_{i=1}^r \lambda_i S_i^\circ - T \sum_{i=r+1}^s \lambda_i (S_i^\circ - C_i^\circ),\end{aligned}\quad (880)$$

where  $\Delta H^\circ$  is the value of  $\Delta H$  at the absolute zero for the given reaction between the species  $1, \dots, r$  in the crystalline state and the species  $r+1, \dots, s$  in the vapour state. The values to be given to  $C_i$ ,  $S_i^\circ$  are those in the crystalline state for the species  $1, \dots, r$ , while the values to be given to  $C_i$ ,  $C_i^\circ$ ,  $S_i^\circ$  are those in the vapour state for the species  $r+1, \dots, s$ . The symbol  $p_i$  denotes the partial vapour pressure of the species  $i$  in the vapour phase.

The equilibrium condition for the given reaction is simply

$$\Delta G = 0. \quad (881)$$

The equilibrium constant  $K$  defined by

$$K = \prod_{i=r+1}^s (p_i)^{\lambda_i}, \quad (882.1)$$

$$\text{or} \quad \log K = \sum_{i=r+1}^s \lambda_i \log p_i, \quad (882.2)$$

is according to (880), (881) and (882) given by

$$\begin{aligned}\log K &= -\frac{\Delta H^\circ}{RT} + \sum_{i=r+1}^s \lambda_i \frac{C_i^\circ}{R} \log T + \int_0^T \frac{dT'}{T'^2} \int_0^T \sum_{i=1}^r \frac{\lambda_i C_i}{R} dT' \\ &\quad + \int_0^T \frac{dT'}{T'^2} \int_0^T \sum_{i=r+1}^s \lambda_i \frac{C_i - C_i^\circ}{R} dT' + I, \quad (883)\end{aligned}$$

where the integration constant  $I$  is given by

$$I = \frac{1}{R} \sum_{i=1}^r \lambda_i S_i^\circ + \frac{1}{R} \sum_{i=r+1}^s \lambda_i (S_i^\circ - C_i^\circ), \quad (884)$$

or using (877)

$$I = \frac{1}{R} [\Delta S^\circ]^s + \sum_{i=r+1}^s \lambda_i i_i, \quad (885)$$

where  $[\Delta S^\circ]^s$  is the value of  $\Delta S^\circ$  for the reaction taking place between crystalline phases only, and  $i_i$  is the chemical constant of the species  $i$ .

If in particular the so-called third law holds good for the particular reaction between the crystalline phases, then

$$[\Delta S^\circ]^s = 0, \quad (886.1)$$

and (885) simplified to

$$I = \sum_i \lambda_i i_i, \quad (886.2)$$

a relation due to Nernst.

When (886.1) and (886.2) are true the equilibrium constant for the reaction can be calculated from purely thermal data, provided one knows the chemical constants of the single gases. This will also, of course, be the case for any reaction between vapours only involving no crystalline phases. It is owing to the relation (886.2) that the constants  $i$  received the name "chemical constants". While the relation (886.2) will often be true it will not hold in those cases where (886.1) is not true. The formula (885) for  $I$  is, on the other hand, of universal validity.

*Predictions from Quantum Theory Concerning  $\Delta S^\circ$ .*—The formulæ so far given are, with the exception of (886.1) and (886.2), purely thermodynamic and so of universal validity. For them to be useful it is necessary to know the values of  $\Delta S^\circ$  for a given reaction or of  $\Delta S^\circ$  for a given species in the crystal and in the vapour. Thermodynamics tells us nothing about these values, but they can be predicted from quantum theory provided sufficient is known concerning the lowest quantum states of each species both in the crystal and in the vapour. As this part of the subject belongs to statistical mechanics and not to thermodynamics, we shall not attempt to treat it in detail. Since, however, the predictions in many cases lead to especially simple results we shall quote some of these. For further details the reader is referred to the published work of Fowler and Sterne and that of Giauque and his collaborators.

*Monatomic Vapours.*—In the case of monatomic vapours behaving as perfect gases the molar heat capacity  $C_P$  has the constant value  $\frac{5}{2}R$  from the lowest attainable temperatures up to quite high temperatures. The reason for this is that in a monatomic gas the three degrees of translational kinetic energy are completely excited and obey the law of equipartition, while as regards all other kinds of energy, such as rotational, vibrational and electronic the atoms are all in their lowest quantum states at all temperatures except exceedingly high ones. For monatomic vapours we therefore have

$$C_P^\circ = \frac{5}{2}R, \quad (887)$$

and in evaluating the integrals  $\int_0^T$  we extrapolate to the absolute zero using the value  $\frac{5}{2}R$  for  $C_P^\circ$ . The value of the vapour pressure constant  $i$  of a monatomic vapour is given according to statistical theory and quantum theory by the formula

$$i = \log \frac{(2\pi M)^{3/2} R^{3/2}}{N^4 h^3} + \log \frac{\varpi^G}{\varpi^S}, \quad (888)$$

where  $N$  is the number of molecules in a mole ("Avogadro's number"),  $R$  is the gas constant,  $h$  is Planck's constant and  $M$  is the molar mass ("atomic weight") of the species,  $\varpi^G$  is the statistical weight of the lowest energy state of the gaseous atom and  $\varpi^S$  is the statistical weight per atom in the crystal in its lowest energy state.

In evaluating the ratio  $\varpi^G/\varpi^S$  it is permissible to ignore nuclear spins as these will contribute the same factor to both  $\varpi^G$  and  $\varpi^S$  and so their effect will cancel.

The lowest energy state of the atoms of the inert gases both in the vapour and in the crystalline state is  $^1S$  with a statistical weight 1 (ignoring nuclear spins). We therefore have

$$\log \frac{\varpi^G}{\varpi^S} = \log \frac{1}{1} = 0. \quad (889)$$

In the atoms of the alkali metals on the other hand the lowest energy level in the vapour state is  $^2S$  with a statistical weight 2 (ignoring nuclear spin). In the crystal on the other hand we have univalent ions in a state  $^1S$  with a statistical weight 1 (ignoring nuclear spins) together with free electrons. The

electrons form a "completely degenerate" perfect gas with a statistical weight unity. For the alkali metals, therefore

$$\log \frac{\varpi^g}{\varpi^s} = \log \frac{2}{1} = \log 2. \quad (890)$$

*Diatomic Vapours other than Hydrogen.*—All diatomic vapours other than hydrogen have two degrees of rotational energy fully excited down to the lowest temperatures attainable. The molar heat capacity  $C_P$  therefore retains the value  $\frac{7}{2}R$  from ordinary temperatures down to the lowest attainable, and we have

$$C_P^o = \frac{7}{2}R. \quad (891)$$

This is the value of  $C_P^o$  to be used in the extrapolation required to evaluate the integrals of the form  $\int_0^T$ . According to quantum theory and statistical theory the vapour pressure constant of a diatomic vapour is then given by

$$i = \log \frac{(2\pi M)^{3/2} R^{1/2}}{N^4 h^3} \frac{8\pi^2 A R}{N h^2} + \log \frac{\varpi^g}{\varpi^s \sigma}, \quad (892)$$

where  $N$  is the number of molecules in one mole ("Avogadro's number"),  $R$  is the gas constant,  $h$  is Planck's constant,  $M$  is the molar mass (molecular weight) and  $A$  the principal moment of inertia of the molecule.  $\varpi^g$  is the statistical weight of the lowest energy state of the gaseous molecule in its lowest energy state, and  $\varpi^s$  is the statistical weight per molecule in the crystal in its lowest energy state,  $\sigma$  is a symmetry number being equal to 2 for a molecule composed of two similar atoms and to 1 otherwise.

In evaluating  $\varpi^g/\varpi^s$  it is permissible to ignore the nuclear spins as these will contribute the same factor to both  $\varpi^g$  and  $\varpi^s$  and so their effects will cancel.

The symmetry number  $\sigma$  occurs because a symmetrical molecule can exist in fewer rotational quantum states than an unsymmetrical one. This is due to the necessity that the eigen-function of all actually occurring quantum states should have the same symmetry property with respect to the two atomic nuclei when these are identical. But one-half the rotational eigen-functions are symmetrical and one-half are anti-symmetrical with respect to the atomic nuclei, and so only half the rotational quantum states are available for a symmetrical



molecule. There is a consequent reduction for symmetrical molecules in the contribution of the rotation to the entropy which can be shown to take the form of the factor  $\frac{1}{2}$  in the argument of the logarithm in (892).

For the hydrogen halides the lowest energy state in both vapour and crystal is  $^1\Sigma$  with a statistical weight 1 (ignoring nuclear spins). For the hydrogen halides we therefore have

$$\log \frac{w^g}{w^{sg}} = \log \frac{1}{1 \cdot 1} = 0. \quad (893)$$

For the halogens and for nitrogen the lowest energy state in both vapour and crystal is  $^1\Sigma$  with a statistical weight 1 (ignoring nuclear spins). For these species we therefore have

$$\log \frac{w^g}{w^{sg}} = \log \frac{1}{1 \cdot 2} = -\log 2. \quad (894)$$

For oxygen in the vapour the lowest energy level is  $^3\Sigma$  with a statistical weight 3 (ignoring nuclear spins). We therefore have

$$\log \frac{w^g}{w^{sg}} = \log \frac{3}{w^s \cdot 2}. \quad (895)$$

The experimental value for  $i$  indicates that the statistical weight of the crystal in its lowest energy state (ignoring nuclear spin) is unity, that is  $w^s$  is unity. This can be explained if in the crystal the molecules  $O_2$  are paired in such a manner that their magnetic moments (or electron spins) cancel. For carbon monoxide the lowest energy level is  $^1\Sigma$  with a statistical weight 1 (ignoring nuclear spins). We should therefore expect to find

$$\log \frac{w^g}{w^{sg}} = \log \frac{1}{1 \cdot 1} = 0. \quad (896)$$

Actually it is found that the vapour pressure constant is less than corresponds to formulæ (892) and (896) by  $\log 2$ . This can be explained on the assumption that in the crystal the molecules of CO may point in either direction. This explanation seems not unlikely as the close resemblance of CO to  $N_2$  in their physical properties indicates that the dissymmetry in the CO molecule is small.

*Isotopes.*—The effect of the existence of isotopes would be quite complicated were it not that, owing to the very small difference in the chemical properties of isotopes, the various isotopes of each element may with a high degree of accuracy

be assumed present in constant proportions in all phases. Thanks to this fact the existence or non-existence of isotopes is entirely without effect on the value of the chemical constant, except in so far as the values of  $M$  and  $A$  are affected. Thus for a mixture of isotopes present in the fractional proportions  $N_r$  of each isotope  $r$ , we should replace (892) by the more exact

$$i = \sum_r N_r \log \frac{(2\pi M_r)^{3/2} R^{3/2}}{N^4 h^3} \frac{8\pi^2 A_r R}{N h^2} + \log \frac{\varpi^\sigma}{\varpi^s \sigma}, \quad (897)$$

where  $M_r$  and  $A_r$  are the values of  $M$  and  $A$  for the isotope  $r$ .

That the presence or absence of isotopes has no further effect may be clearly seen by comparing the vapour pressure constants of  $\text{Cl}_{35} - \text{Cl}_{35}$  and  $\text{Cl}_{35} - \text{Cl}_{37}$  with those of  $\text{N}_2$  and  $\text{CO}$ . For the unsymmetrical molecules  $\text{Cl}_{35} - \text{Cl}_{37}$  and  $\text{CO}$  the number of rotational quantum states in the vapour is greater than for the symmetrical molecules  $\text{Cl}_{35} - \text{Cl}_{35}$  and  $\text{N}_2$  and so  $\sigma$  has the value 1 for the former and 2 for the latter. But this effect is exactly cancelled by a doubling in the value of  $\varpi^s$  for the unsymmetrical molecules owing to the possibility of two effectively equally probable orientations of the molecule in the crystal. The value of  $\varpi^s \sigma$  is thus the same for  $\text{Cl}_{35} - \text{Cl}_{35}$  as for  $\text{Cl}_{35} - \text{Cl}_{37}$ .

*Hydrogen.*—The species hydrogen is peculiar and probably unique in two respects. Firstly, owing to the small moment of inertia of the molecule, the two rotational degrees of freedom are no longer fully excited at low temperatures and at the lowest attainable temperatures they are practically unexcited. If, then, we evaluate the integrals of the form  $\int_0^T$  by extrapolation from the lowest temperatures accessible to experiment, we have to use

$$C_P^\circ = \frac{5}{2}R, \quad (898)$$

the same as for monatomic vapours and unlike other diatomic vapours. Secondly, the hydrogen molecules *in the crystal*, unlike those of any other diatomic molecules, are in a state of rotation down to the lowest attainable temperatures. Thus at the lowest attainable temperatures the states of the molecules in the vapour and those of the molecules in the crystal differ only by their translational motion. Statistical mechanics, therefore, leads to the formula for  $i$

$$i = \log \frac{(2\pi M)^{3/2} R^{3/2}}{N^4 h^3}, \quad (899)$$

of the same form as for a monatomic gas in a  $^1S$  state such as one of the inert gases. Formula (899) is to be used in conjunction with (898).

When considering equilibria involving hydrogen at ordinary or high temperatures it is sometimes more convenient to use a treatment more analogous to that of other diatomic gases. We may do this if we evaluate the integrals of the form  $\int_0^T$  by extrapolating down to the absolute zero from the temperatures where  $C_P$  has the value  $\frac{7}{2}R$  using the value

$$C_P^0 = \frac{7}{2}R, \quad (900)$$

and ignoring the fact that  $C_P$  actually falls to lower values in the range of temperature over which we are extrapolating. Corresponding to formula (900) we have for  $i$

$$i = \log \frac{(2\pi M)^{3/2} R^{5/2}}{N^4 h^3} \frac{8\pi^2 A R}{N h^2} + \log \frac{\varpi^g}{\varpi^s \sigma}, \quad (901)$$

where,  $H_2$  being a symmetrical molecule,  $\sigma$  has the value 2. In order to evaluate the ratio  $\varpi^g/\varpi^s$  we have to make use of the knowledge that the hydrogen nucleus has a spin of  $1/2$  unit of  $h/2\pi$ . It follows from the existence of this nuclear spin that there are two kinds of hydrogen molecules, those antisymmetrical in the nuclear spins, called "para-hydrogen," and those symmetrical in the nuclear spins, called "ortho-hydrogen". The latter exist in three times as many states as the former. It follows that at high, and in fact ordinary, temperatures the equilibrium ratio between para-hydrogen and ortho-hydrogen is 1 to 3. The change from one form to the other is under normal conditions extremely slow, and so we may regard all hydrogen under normal experimental conditions both *at high and at low temperatures* as a 1 to 3 mixture of para-hydrogen to ortho-hydrogen. According to this viewpoint we shall have for  $\varpi^s$

$$\varpi^s = (\varpi^P)^{1/4} \cdot (\varpi^o)^{3/4}, \quad (902)$$

where  $\varpi^P$  and  $\varpi^o$  are the statistical weights of the lowest quantum states for para-hydrogen and ortho-hydrogen respectively. These values are

$$\varpi^P = 1 \quad \varpi^o = 3. \quad (903)$$

Substituting (903) into (902) we obtain

$$\log \varpi^s = \frac{3}{4} \log 3. \quad (904)$$

For  $\varpi^G$  we have to use the statistical weight of the lowest energy level of hydrogen in the vapour. This energy level is the lowest level of para-hydrogen and has a statistical weight 1,

$$\varpi^G = 1. \quad (905)$$

We therefore obtain finally

$$\log \frac{\varpi^G}{\varpi^S \sigma} = -\frac{3}{4} \log 3 - \log 2. \quad (906)$$

This formula to be used in conjunction with formula (900) for  $C_P^\circ$ .

*Vapours with Polyatomic Linear Molecules.*—Polyatomic linear molecules such as  $\text{CO}_2$  and  $\text{N}_2\text{O}$  have at ordinary and low temperatures the same fully excited degrees of freedom as diatomic molecules. We may therefore use the same formulæ as for diatomic molecules, namely

$$C_P^\circ = \frac{7}{2}R \quad (907)$$

$$i = \log \frac{(2\pi M)^{3/2} R^{3/2}}{N^4 h^3} \frac{8\pi^2 A R}{N h^2} + \log \frac{\varpi^G}{\varpi^S \sigma}, \quad (908)$$

with the same notation as for diatomic molecules.  $\sigma$  will have the value 2 for the symmetrical molecule  $\text{OCO}$ , but 1 for the molecule  $\text{N}_2\text{O}$  on the assumption that its structure is  $\text{NNO}$ .

*Vapours with Polyatomic Non-Linear Molecules.*—Polyatomic non-linear molecules have altogether six degrees of freedom completely excited down to the lowest attainable temperatures. Consequently the value of  $C_P^\circ$  is given by

$$C_P^\circ = 4R. \quad (909)$$

The value given for the vapour pressure constant  $i$  by statistical theory and quantum theory is then

$$i = \log \frac{(2\pi M)^{3/2} R^{3/2}}{N^4 h^2} \frac{8\pi^2 (2\pi)^{3/2} (ABC)^{1/2} R^{3/2}}{N^3 h^3} + \log \frac{\varpi^G}{\varpi^S \sigma}, \quad (910)$$

where  $A$ ,  $B$ ,  $C$  are the three principal moments of inertia of the molecule.  $\varpi^G$  is the statistical weight of the lowest energy state in the vapour and  $\varpi^S$  the statistical weight per atom in the crystal in its state of lowest energy.  $\sigma$  is a symmetry number depending on the arrangement of similar atoms in the molecule.

The classification of the quantum states of polyatomic molecules is complicated and the values of  $\varpi^G$  and  $\varpi^S$  will not

be discussed here. We will only mention that for many molecules in which all the atoms have their normal valencies, as in the majority of organic compounds the value of  $w^G/w^S\sigma$  may be expected to be either 1 or  $\frac{1}{2}$  according as to whether the molecule has one or two effectively equally probable directions of orientation in the crystal.

*So-called Absolute Entropies.*—In our discussion we have followed Fowler in referring only to the difference in entropy or partial molar entropy between two states, never to the absolute value of either in a given state. The value that can be assigned to the latter is arbitrary. Some authors, in particular Planck, G. N. Lewis and Giauque, adopt the convention that the entropy of each element in a perfect crystalline state at the absolute zero is zero, and they call the entropy referred to this zero "absolute entropy". There is no objection to this conventional choice of zero entropy, but there is nothing "absolute" about it. If an element consists of several isotopes its entropy at the absolute zero will be greater than that of a crystal consisting of a pure isotope. To determine this difference it is not sufficient to know the proportions of isotopes of each atomic mass, because there is the possibility of several isotopes with equal atomic mass ("isobaric isotopes"). Knowledge on this point is usually not available. A second objection is that since transmutation of elements is now known to be possible the entropies of the various elements are not independent of one another. The only rational system of absolute entropies would be referred to certain standard states of nuclei and protons. It is hardly necessary to state that the use of such a system is not feasible owing to lack of data on the entropy changes in transmutation. Even if feasible, it is doubtful whether it would serve any useful purpose.

#### NOTES AND REFERENCES

The whole subject of the so-called "third law" and vapour pressure constants is treated in detail from the point of view of quantum theory and statistical mechanics by Fowler and Sterne in *Reviews of Modern Physics*, 4, 635 (1932) where references are given to earlier work. The present chapter is an attempt to summarise the thermodynamic significance of their conclusions. This subject has also been studied extensively both on the theoretical and on the experimental side by Giauque and his collaborators. Their work is published in numerous papers in the *J. Am. Chem. Soc.* (1928) to (1932).

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